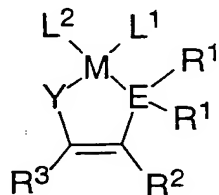


## Emulsion polymerization of olefins

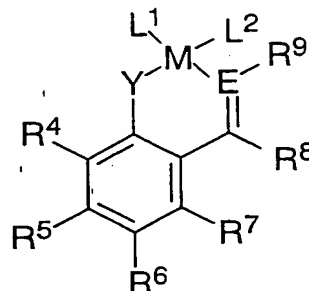
The present invention relates to a process for emulsion  
 5 polymerizing one or more olefins by reacting the olefins with a  
 complex compound of the formula Ia or Ib or with a mixture of the  
 complex compounds Ia and Ib

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Ia



Ib

20 where:

- M is a transition metal from groups 7 to 10 of the Periodic Table of the Elements;
- 25 L<sup>1</sup> is phosphines (R<sup>16</sup>)<sub>x</sub>PH<sub>3-x</sub> or amines (R<sup>16</sup>)<sub>x</sub>NH<sub>3-x</sub> with identical or different radicals R<sup>16</sup>, ethers (R<sup>16</sup>)<sub>2</sub>O, H<sub>2</sub>O, alcohols (R<sup>16</sup>)OH, pyridine, pyridine derivatives of the formula C<sub>5</sub>H<sub>5-x</sub>(R<sup>16</sup>)<sub>x</sub>N, CO, C<sub>1</sub>-C<sub>12</sub> alkyl nitriles, C<sub>6</sub>-C<sub>14</sub> aryl nitriles or ethylenically unsaturated double bond systems, x being an integer from 0 to 3,
- 30 L<sup>2</sup> is halide ions, amide ions R<sub>h</sub>NH<sub>2-h</sub>, h being an integer from 0 to 2, and also C<sub>1</sub>-C<sub>6</sub> alkyl anions, allyl anions, benzyl anions or aryl anions, it being possible for L<sup>1</sup> and L<sup>2</sup> to be linked to one another by one or more covalent bonds,
- 35 E is nitrogen, phosphorus, arsenic or antimony,  
 X is -SO<sub>3</sub><sup>-</sup>, -O-PO<sub>3</sub><sup>2-</sup>, NH(R<sup>15</sup>)<sub>2</sub><sup>+</sup>, N(R<sup>15</sup>)<sub>3</sub><sup>+</sup> or -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OH,  
 n is an integer from 0 to 15,  
 Y is oxygen, sulfur, N-R<sup>10</sup> or P-R<sup>10</sup>,  
 R<sup>1</sup> is hydrogen, C<sub>1</sub>-C<sub>12</sub> alkyl groups, C<sub>7</sub>-C<sub>13</sub> aralkyl radicals  
 40 and C<sub>6</sub>-C<sub>14</sub> aryl groups, unsubstituted or substituted by a hydrophilic group X,  
 R<sup>2</sup> and R<sup>3</sup> are hydrogen,  
 hydrophilic groups X,  
 C<sub>1</sub>-C<sub>12</sub> alkyl, it being possible for the alkyl groups to  
 45 be branched or unbranched,  
 C<sub>1</sub>-C<sub>12</sub> alkyl substituted one or more times by identical or different substituents comprising C<sub>1</sub>-C<sub>12</sub> alkyl

groups, halogens, hydrophilic groups X, C<sub>1</sub>-C<sub>12</sub> alkoxy groups or C<sub>1</sub>-C<sub>12</sub> thioether groups, C<sub>7</sub>-C<sub>13</sub> aralkyl, C<sub>3</sub>-C<sub>12</sub> cycloalkyl,

5 C<sub>3</sub>-C<sub>12</sub> cycloalkyl substituted one or more times by identical or different substituents comprising C<sub>1</sub>-C<sub>12</sub> alkyl groups, halogens, hydrophilic groups X, C<sub>1</sub>-C<sub>12</sub> alkoxy groups or C<sub>1</sub>-C<sub>12</sub> thioether groups, C<sub>6</sub>-C<sub>14</sub> aryl,

10 C<sub>6</sub>-C<sub>14</sub> aryl substituted one or more times by identical or different substituents comprising C<sub>1</sub>-C<sub>12</sub> alkyl groups, halogens, hydrophilic groups X, monohalogenated or polyhalogenated C<sub>1</sub>-C<sub>12</sub> alkyl groups, C<sub>1</sub>-C<sub>12</sub> alkoxy groups, silyloxy groups OSiR<sup>10</sup>R<sup>11</sup>R<sup>12</sup>, amino groups NR<sup>13</sup>R<sup>14</sup> or C<sub>1</sub>-C<sub>12</sub> thioether groups,

15 C<sub>1</sub>-C<sub>12</sub> alkoxy groups, silyloxy groups OSiR<sup>10</sup>R<sup>11</sup>R<sup>12</sup>, halogens or amino groups NR<sup>13</sup>R<sup>14</sup>,

20 it being possible for the radicals R<sup>2</sup> and R<sup>3</sup> together to form a saturated or unsaturated 5- to 8-membered ring, and at least one radical R<sup>1</sup>, R<sup>2</sup> or R<sup>3</sup> carrying a hydrophilic group X;

25 R<sup>4</sup> to R<sup>7</sup> are hydrogen, hydrophilic groups X; C<sub>1</sub>-C<sub>12</sub> alkyl, it being possible for the alkyl groups to be branched or unbranched, C<sub>1</sub>-C<sub>12</sub> alkyl, substituted one or more times by identical

30 or different substituents comprising C<sub>1</sub>-C<sub>12</sub> alkyl groups, halogens, hydrophilic groups X, C<sub>1</sub>-C<sub>12</sub> alkoxy groups or C<sub>1</sub>-C<sub>12</sub> thioether groups, C<sub>7</sub>-C<sub>13</sub> aralkyl, C<sub>3</sub>-C<sub>12</sub> cycloalkyl,

35 C<sub>3</sub>-C<sub>12</sub> cycloalkyl substituted one or more times by identical or different substituents comprising C<sub>1</sub>-C<sub>12</sub> alkyl groups, halogens, hydrophilic groups X, C<sub>1</sub>-C<sub>12</sub> alkoxy groups or C<sub>1</sub>-C<sub>12</sub> thioether groups, C<sub>6</sub>-C<sub>14</sub> aryl,

40 C<sub>6</sub>-C<sub>14</sub> aryl substituted one or more times by identical or different substituents comprising C<sub>1</sub>-C<sub>12</sub> alkyl groups, halogens, hydrophilic groups X, monohalogenated or polyhalogenated C<sub>1</sub>-C<sub>12</sub> alkyl groups, C<sub>1</sub>-C<sub>12</sub> alkoxy groups, silyloxy groups OSiR<sup>10</sup>R<sup>11</sup>R<sup>12</sup>, amino groups NR<sup>13</sup>R<sup>14</sup> or C<sub>1</sub>-C<sub>12</sub> thioether groups,

45 C<sub>1</sub>-C<sub>12</sub> alkoxy groups, silyloxy groups OSiR<sup>10</sup>R<sup>11</sup>R<sup>12</sup>,

- halogens,  
NO<sub>2</sub> groups  
or amino groups NR<sup>13</sup>R<sup>14</sup>,  
it being possible for pairs of adjacent radicals R<sup>4</sup> to  
5 R<sup>7</sup> together to form a saturated or unsaturated  
5-8-membered ring,  
R<sup>8</sup> and R<sup>9</sup> are hydrogen, C<sub>1</sub>-C<sub>6</sub> alkyl groups, C<sub>7</sub>-C<sub>13</sub> aralkyl groups  
and C<sub>6</sub>-C<sub>14</sub> aryl groups, unsubstituted or substituted by  
a hydrophilic group X,  
10 R<sup>10</sup> to R<sup>15</sup> are hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl groups, which may be  
substituted in turn by O(C<sub>1</sub>-C<sub>6</sub> alkyl) or N(C<sub>1</sub>-C<sub>6</sub> alkyl)<sub>2</sub>  
groups, or are C<sub>3</sub>-C<sub>12</sub> cycloalkyl groups, C<sub>7</sub>-C<sub>13</sub> aralkyl  
radicals and C<sub>6</sub>-C<sub>14</sub> aryl groups;  
R<sup>16</sup> is hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl groups, which may in turn be  
15 substituted by O(C<sub>1</sub>-C<sub>6</sub> alkyl) or N(C<sub>1</sub>-C<sub>6</sub> alkyl)<sub>2</sub> groups,  
or is C<sub>3</sub>-C<sub>12</sub> cycloalkyl groups, C<sub>7</sub>-C<sub>13</sub> aralkyl radicals  
and C<sub>6</sub>-C<sub>14</sub> aryl groups unsubstituted or substituted by a  
hydrophilic group X,  
20 in water or in a solvent mixture containing at least 50% by  
volume of water, optionally in the presence of an activator and  
an emulsifier.

The compounds Ia and Ib are used in a ratio of from 0:100 to  
25 100:0 mol%. For the process of the invention an activator such as  
olefin complexes of rhodium or of nickel, for example, is  
optionally used. This invention further relates to dispersions of  
polyolefins such as polyethylene and ethylene copolymers, for  
example, in water, and to the use of the aqueous dispersions of  
30 the invention for paper applications such as paper coating or  
surface sizing, paints, adhesive base materials, molded foams  
such as mattresses, textile and leather applications, carpet back  
coatings, or pharmaceutical applications.

35 Aqueous dispersions of polymers are used commercially in numerous  
very different applications. Examples that may be mentioned  
include paper applications (coating and surface sizing), raw  
materials for paints and varnishes, adhesive base materials  
(including pressure-sensitive adhesives), textile and leather  
40 applications, chemicals for the construction industry, molded  
foams (mattresses, carpet back coatings), and for medical and  
pharmaceutical products, as binders for preparations, for  
example. A compilation is given in D. Distler (editor) "Wäßrige  
Polymerdispersionen", Wiley-VCH Verlag, 1st edition, 1999.

To date it has been difficult to prepare aqueous dispersions of polyolefins. However, it would be desirable to be able to provide such aqueous polyolefin dispersions since the monomers such as ethylene or propylene are highly advantageous from economic standpoints.

Current processes for preparing aqueous dispersions of this kind from the corresponding olefins make use either of free-radical high-pressure polymerization or else of the preparation of secondary dispersions. These processes are hampered by disadvantages. The free-radical polymerization processes require extremely high pressures and are restricted on the industrial scale to ethylene and ethylene copolymers, and the necessary apparatus is very expensive to purchase and maintain (F. Rodriguez, Principles of Polymer Systems, 2<sup>nd</sup> edition, McGraw-Hill, Singapore 1983, p. 384). An alternative possibility is first to polymerize ethylene by whatever process and then to prepare a secondary dispersion, as described in US 5,574,091. This method is a multistage process and is therefore very laborious.

For the above reasons it is desirable to polymerize 1-olefins such as ethylene or propylene under the conditions of emulsion polymerization and to prepare the required dispersion in one step from the corresponding monomer. Furthermore, emulsion polymerization processes have the advantage in very general terms that they give polymers having higher molecular masses, in a process which facilitates heat dissipation. Finally, reactions in aqueous systems are of interest in very general terms because water is an inexpensive and environmentally friendly solvent.

However, no satisfactory process has yet been found for the polymerization of 1-olefins such as ethylene or propylene. The problem lies in general in the catalyst required to polymerize these monomers.

Olefins may be polymerized using electrophilic transition metal compounds such as  $\text{TiCl}_4$  (Ziegler-Natta catalyst) or metallocenes, as described for example by H.-H. Brintzinger et al. in *Angew. Chem.* 1995, 107, 1255, *Angew. Chem., Int. Ed. Engl.* 1995, 34, 1143. However, both  $\text{TiCl}_4$  and metallocenes are sensitive to moisture and are therefore poorly suited to preparing polyolefins in emulsion polymerization. The aluminum alkyls used as cocatalysts are also moisture sensitive, with the consequence that water as a catalyst poison must be carefully excluded.

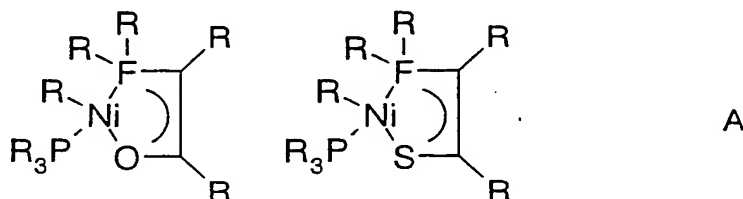
There are only a few reports of transition metal catalyzed reactions of ethylene in an aqueous medium. For instance, L. Wang et al. in *J. Am. Chem. Soc.* 1993, 115, 6999 report on a rhodium catalyzed polymerization. However, at around one insertion/hour, the activity is much too low for industrial applications.

The reaction of ethylene with nickel P,O chelate complexes appears much more promising, as described in U.S. Patents US 3,635,937, US 3,637,636, US 3,661,803, and US 3,686,159. No polymer analysis data are reported. Furthermore, the reported activity is still too low for industrial applications.

EP-A 0 046 331 and EP-A 0 046 328 report on the reaction of ethylene with Ni chelate complexes of the formula A

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where R is identical or different organic substituents of which one carries a sulfonyl group, and F is phosphorus, arsenic or nitrogen. Under the chosen reaction conditions in solvents such as methanol or mixtures of methanol and a hydrocarbon, only oligomers are obtained, which are unsuitable for the abovementioned applications. The advantage of the sulfonated derivatives over unsulfonated compounds, as described by W. Keim et al. in *Angew. Chem.* 1978, 90, 493; *Angew. Chem., Int. Ed. Engl.* 1978, 6, 466, lay in their greater activity.

In US 4,698,403 (column 7, lines 13-18) and in US 4,716,205 (column 6, lines 59-64) it is shown that an excess of water acts as a catalyst poison to bidentate Ni chelate complexes even if they carry a  $\text{SO}_3^-$  group.

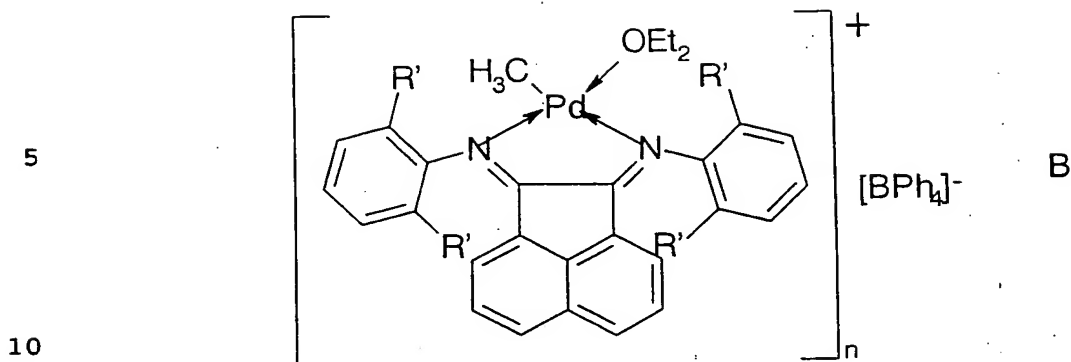
From the documents cited above it is evident that numerous Ni complexes are not polymerization-active in the presence of water.

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On the other hand, it is known from WO 97/17380 that palladium compounds of the formula B

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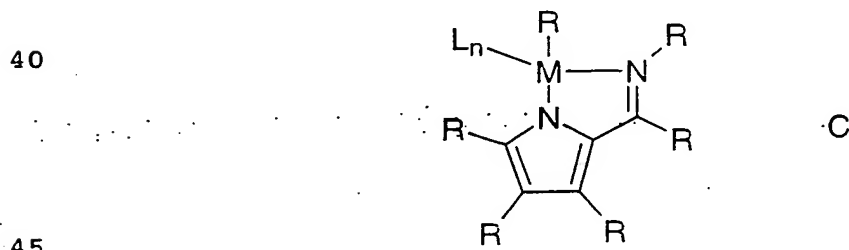


Et = C<sub>2</sub>H<sub>5</sub>, Ph = Phenyl

15 where R' is, for example, isopropyl groups, or the analogous  
nickel compounds, are able to polymerize higher olefins such as  
1-octene in an aqueous environment. Optionally, an emulsifier may  
be added in order to facilitate the polymerization. However, it  
is noted that the temperature of 40°C ought not to be exceeded,  
20 since otherwise the catalyst is deactivated (p. 25, line 5 et  
seq.). Higher reaction temperatures are, however, desirable in  
general since they make it possible to increase the activity of a  
catalyst system.

25 Further disadvantages of catalyst systems of the formula B are  
that with ethylene, in general, highly branched polymers are  
formed (L.K. Johnson *J. Am. Chem. Soc.* 1995, 117, 6414; C.  
Killian, *J. Am. Chem. Soc.* 1996, 118, 11664), which to date have  
been of fairly minor industrial importance, and with higher  
30 α-olefins (L.T. Nelson *Polymer Preprints* 1997, 38, 133) so-called  
chain running of the active complexes has been an unavoidable  
observation. This chain running results in a large number of  
1,ω-misinsertions, as a result of which amorphous polymers are  
generally produced whose suitability as materials of construction  
35 is low.

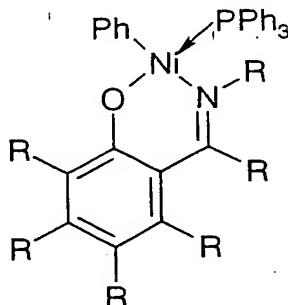
It is also known that complexes of the formula C



(WO 98/42665) where M = Ni or Pd and with n neutral ligands L are polymerization-active in the presence of small amounts of water without suffering losses in catalytic activity (p. 16, line 13). However, these amounts of water must not exceed 100 equivalents, based on the complex (page 16, lines 30-31). It is not possible to conduct an emulsion polymerization under these conditions.

It is further known that complexes of the formula D

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D

Ph = phenyl

20 with identical or different radicals R are also able to polymerize ethylene in the presence of small amounts of water (WO 98/42664, especially page 17, line 14 et seq.). However, these amounts of water must not exceed 100 equivalents, based on the complex (page 17, lines 33-35). It is impossible, however, to  
25 conduct an emulsion polymerization under these conditions.

It is an object of the present invention to provide a process which

- 30 - polymerizes olefins to polyolefins in the presence of large amounts of water,  
- produces materials of construction with minimal branching and with high molecular weights, and  
- permits this reaction to be conducted under industrially  
35 reasonable conditions.

A further object of the present invention was to use the process of the invention

- 40 - to prepare aqueous polyolefin dispersions, and  
- to use these polyolefin dispersions for paper applications (coating and surface sizing), raw materials for paints and varnishes, adhesive base materials (including pressure-sensitive adhesives), textile and leather applications,  
45 chemicals for the construction industry, molded foams

(mattresses, carpet back coatings), and for medical and pharmaceutical products.

We have found that this object is achieved and that complex systems comprising at least one compound of the formula Ia or Ib are outstandingly suitable for polymerizing one or more olefins in emulsion polymerization processes.

Suitable olefins for polymerization that may be mentioned include the following: ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene and 1-eicosene, and also branched olefins such as 4-methyl-1-pentene, vinylcyclohexene and vinylcyclohexane, and also styrene, *para*-methylstyrene and *para*-vinylpyridine, preference being given to ethylene and propylene. Ethylene is particularly preferred.

The copolymerization of two olefins also takes place successfully with the process of the invention, it being possible to select the comonomer from the following groups:

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- 1-olefins such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene and 1-eicosene, and also branched olefins such as 4-methyl-1-pentene, vinylcyclohexene and vinylcyclohexane, as well as styrene, *para*-methylstyrene and *para*-vinylpyridine, preference being given to propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, and 1-decene;

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- internal olefins such as norbornene, norbornadiene or *cis*- or *trans*-2-butene;

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- polar monomers such as acrylic acid, acrylic acid C<sub>1</sub>-C<sub>8</sub> alkyl esters, 2-hydroxyethyl acrylate, 3-hydroxypropyl acrylate, 4-hydroxybutyl acrylate, methacrylic acid, methacrylic acid C<sub>1</sub>-C<sub>8</sub> alkyl esters, C<sub>1</sub>-C<sub>6</sub> alkyl vinyl ethers, and vinyl acetate; preference is given to acrylic acid, methyl

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acrylate, ethyl acrylate, *n*-butyl acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, methyl methacrylate, ethyl methacrylate, *n*-butyl methacrylate, ethyl vinyl ether, and vinyl acetate.

The ratio of the two monomers may be chosen freely. Preferred comonomers are 1-olefins and polar monomers. However, it is preferred to use the comonomer in proportions of from 0.1 to 20 mol%, based on the principal monomer.

In the complex compounds of the formulae Ia and Ib, the radicals are defined as follows:



- M is a transition metal from groups 7 to 10 of the Periodic Table of the Elements, preferably manganese, iron, cobalt, nickel or palladium, and with particular preference nickel.
- 5 L<sup>1</sup> is selected from phosphines of the formula (R<sup>16</sup>)<sub>x</sub>PH<sub>3-x</sub> or amines of the formula (R<sup>16</sup>)<sub>x</sub>NH<sub>3-x</sub>, where x is an integer between 0 and 3. However, ethers (R<sup>16</sup>)<sub>2</sub>O such as diethyl ether or tetrahydrofuran, H<sub>2</sub>O, alcohols (R<sup>16</sup>)OH such as methanol or ethanol, pyridine, pyridine derivatives of the formula C<sub>5</sub>H<sub>5-x</sub>(R<sup>16</sup>)<sub>x</sub>N, such as 2-picoline, 3-picoline, 4-picoline, 2,3-lutidine, 2,4-lutidine, 2,5-lutidine, 2,6-lutidine or 3,5-lutidine, CO, C<sub>1</sub>-C<sub>12</sub> alkyl nitriles or C<sub>6</sub>-C<sub>14</sub> aryl nitriles, such as acetonitrile, propionitrile, butyronitrile or benzonitrile, may also be chosen. It is also possible to use mono- or polyethylenically unsaturated double bond systems as the ligand L<sup>1</sup>, such as ethenyl, propenyl, cis-2-butenyl, trans-2-butenyl, cyclohexenyl or norbornenyl.
- 10 20 L<sup>2</sup> is selected from
- halide ions such as fluoride, chloride, bromide, or iodide, preferably chloride or bromide,
  - amide ions (R<sup>16</sup>)<sub>h</sub>NH<sub>2-h</sub>, h being an integer between 0 and 3,
  - 25 - C<sub>1</sub>-C<sub>6</sub> alkyl anions, such as Me<sup>-</sup>, (C<sub>2</sub>H<sub>5</sub>)<sup>-</sup>, (C<sub>3</sub>H<sub>7</sub>)<sup>-</sup>, (n-C<sub>4</sub>H<sub>9</sub>)<sup>-</sup>, (tert-C<sub>4</sub>H<sub>9</sub>)<sup>-</sup> or (C<sub>6</sub>H<sub>14</sub>)<sup>-</sup>;
  - allyl anions or methallyl anions,
  - benzyl anions, or
  - aryl anions such as (C<sub>6</sub>H<sub>5</sub>)<sup>-</sup>.
- 30 In one particular embodiment, L<sup>1</sup> and L<sup>2</sup> are linked to one another by one or more covalent bonds. Examples of such ligands are 1,5-cyclooctadienyl (COD) ligands, 1,6-cyclodecenyl ligands, or 1,5,9-all-trans-cyclododecatrienyl ligands.
- 35 In another particular embodiment, L<sup>1</sup> is tetramethylethylenediamine, only one nitrogen being coordinated with the nickel.
- E is nitrogen, phosphorus, arsenic or antimony, nitrogen and phosphorus being preferred.
- 40 X is selected from -SO<sub>3</sub><sup>-</sup>, -O-PO<sub>3</sub><sup>2-</sup>, NH(R<sup>15</sup>)<sub>2</sub><sup>+</sup>, N(R<sup>15</sup>)<sub>3</sub><sup>+</sup> or -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OH, n being an integer between 1 and 15, preferably from 2 to 10 and with particular preference from 3 to 8.
- 45 Y is oxygen, sulfur, N-R<sup>10</sup> or P-R<sup>10</sup>, oxygen and sulfur being preferred;
- R<sup>1</sup> is selected from

- hydrogen,
- $C_1$ - $C_{12}$  alkyl groups unsubstituted or substituted by a hydrophilic group X; examples of unsubstituted  $C_1$ - $C_{12}$  alkyl groups are methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, sec-pentyl, neo-pentyl, 1,2-dimethylpropyl, iso-amyl, n-hexyl, iso-hexyl, sec-hexyl, n-heptyl, iso-heptyl, n-octyl, n-nonyl, n-decyl, and n-dodecyl; preferably  $C_1$ - $C_6$  alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, sec-pentyl, neo-pentyl, 1,2-dimethylpropyl, iso-amyl, n-hexyl, iso-hexyl, sec-hexyl, with particular preference  $C_1$ - $C_4$  alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl and tert-butyl.
- Examples of the  $C_1$ - $C_{12}$  alkyl groups substituted by a hydrophilic group X are  $CH_2-SO_3^-$ ,  $CH_2-CH_2-SO_3^-$ ,  $-(CH_2)_{10}-SO_3^-$ ,  $-(CH_2)_{12}-SO_3^-$ ,  $-(CH_2)_{16}-SO_3^-$ ,  $-(CH_2)_{18}-SO_3^-$ ,  $-CH_2-NMe_3^+$ ,  $-(CH_2)_{10}-NMe_3^+$ ,  $-(CH_2)_{12}-NMe_3^+$ ,  $-(CH_2)_{16}-NMe_3^+$ ,  $-(CH_2)_{18}-NMe_3^+$ ,  $CH_2-O-CH_2-CH_2-OH$ ,  $CH_2-O-(CH_2-CH_2)_2-OH$ ,  $CH_2-O-(CH_2-CH_2)_3-OH$ ,  $CH_2-O-(CH_2-CH_2)_4-OH$ ,  $CH_2-O-(CH_2-CH_2)_5-OH$ ,  $CH_2-O-(CH_2-CH_2)_6-OH$ , or  $CH_2-O-(CH_2-CH_2)_8-OH$ ;
- $C_7$ - $C_{13}$  aralkyl radicals unsubstituted or substituted by a hydrophilic group X; examples of unsubstituted aralkyl radicals are  $C_7$  to  $C_{12}$  phenylalkyl such as benzyl, 1-phenethyl, 2-phenethyl, 1-phenylpropyl, 2-phenylpropyl, 3-phenylpropyl, neophyl (1-methyl-1-phenylethyl), 1-phenylbutyl, 2-phenylbutyl, 3-phenylbutyl and 4-phenylbutyl, with particular preference benzyl; preferred examples of the aralkyl radicals substituted by a hydrophilic group X are meta-benzylsulfonate, para-benzylsulfonate, ortho- $HO(CH_2CH_2)_n-O$ -benzyl, meta- $HO(CH_2CH_2)_n-O$ -benzyl and para- $HO(CH_2CH_2)_n-O$ -benzyl, n being an integer between 1 and 15, preferably from 2 to 10 and with particular preference from 3 to 8.
- $C_6$ - $C_{14}$  aryl groups, unsubstituted or substituted by a hydrophilic group X. Examples of unsubstituted  $C_6$ - $C_{14}$  aryl groups are phenyl, 1-naphthyl, 2-naphthyl, 1-anthryl, 2-anthryl, 9-anthryl, 1-phenanthryl, 2-phenanthryl, 3-phenanthryl, 4-phenanthryl and 9-phenanthryl, preferably phenyl,

1-naphthyl and 2-naphthyl, with particular preference phenyl. Examples of C<sub>6</sub>-C<sub>14</sub> aryl groups substituted by hydrophilic groups X are

5 meta-benzosulfonate, ortho-benzosulfonate, para-benzosulfonate,  $\alpha$ -(4-naphthosulfonate),  $\beta$ -(4-naphthosulfonate), ortho-HO(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-O-phenyl, meta-HO(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-O-phenyl and para-HO(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-O-phenyl, n being an integer between 1 and 15, preferably from 2 to 10 and with particular

10 preference from 3 to 8.

R<sup>2</sup> and R<sup>3</sup> are:

- hydrogen,
- 15 - hydrophilic groups X,
- C<sub>1</sub>-C<sub>12</sub> alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, sec-pentyl, neo-pentyl, 1,2-dimethylpropyl, iso-amyl, n-hexyl,
- 20 iso-hexyl, sec-hexyl, n-heptyl, iso-heptyl, n-octyl, n-nonyl, n-decyl, and n-dodecyl; preferably C<sub>1</sub>-C<sub>6</sub> alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl,
- 25 sec-pentyl, neo-pentyl, 1,2-dimethylpropyl, iso-amyl, n-hexyl, iso-hexyl, sec-hexyl, with particular preference C<sub>1</sub>-C<sub>4</sub> alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl and tert-butyl,
- 30 - C<sub>1</sub>-C<sub>12</sub> alkyl groups in turn substituted by a hydrophilic group X; examples are CH<sub>2</sub>-CH<sub>2</sub>-SO<sub>3</sub><sup>-</sup>, -(CH<sub>2</sub>)<sub>10</sub>-SO<sub>3</sub><sup>-</sup>, -(CH<sub>2</sub>)<sub>12</sub>-SO<sub>3</sub><sup>-</sup>, -(CH<sub>2</sub>)<sub>16</sub>-SO<sub>3</sub><sup>-</sup>, -(CH<sub>2</sub>)<sub>18</sub>-SO<sub>3</sub><sup>-</sup>, -CH<sub>2</sub>-NMe<sub>3</sub><sup>+</sup>, -(CH<sub>2</sub>)<sub>10</sub>-NMe<sub>3</sub><sup>+</sup>, -(CH<sub>2</sub>)<sub>12</sub>-NMe<sub>3</sub><sup>+</sup>, -(CH<sub>2</sub>)<sub>16</sub>-NMe<sub>3</sub><sup>+</sup>, -(CH<sub>2</sub>)<sub>18</sub>-NMe<sub>3</sub><sup>+</sup>,
- 35 CH<sub>2</sub>-(O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>2</sub>-OH, -CH<sub>2</sub>-(O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>3</sub>-OH, CH<sub>2</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>)<sub>4</sub>-OH, -O-(CH<sub>2</sub>-CH<sub>2</sub>)<sub>5</sub>-OH, CH<sub>2</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>)<sub>6</sub>-OH or CH<sub>2</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>)<sub>8</sub>-OH
- C<sub>1</sub>-C<sub>12</sub> alkyl substituted one or more times by identical or different substituents from the group
- 40 consisting of halogens, C<sub>1</sub>-C<sub>12</sub> alkoxy groups and C<sub>1</sub>-C<sub>12</sub> thioether groups, these groups being as defined above;
- C<sub>7</sub>-C<sub>13</sub> aralkyl, preferably C<sub>7</sub> to C<sub>12</sub> phenylalkyl such as benzyl, 1-phenethyl, 2-phenethyl,
- 45 1-phenylpropyl, 2-phenylpropyl, 3-phenylpropyl,

neophyl (1-methyl-1-phenylethyl), 1-phenylbutyl, 2-phenylbutyl, 3-phenylbutyl and 4-phenylbutyl, with particular preference benzyl;

- 5        - C<sub>3</sub>-C<sub>12</sub> cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl and cyclododecyl; cyclopentyl, cyclohexyl and cycloheptyl are preferred;
- 10       - among the substituted cycloalkyl groups, mention may be made by way of example of the following:
  - 15           2-methylcyclopentyl, 3-methylcyclopentyl, cis-2,4-dimethylcyclopentyl, trans-2,4-dimethylcyclopentyl, 2,2,4,4-tetramethylcyclopentyl, 2-methylcyclohexyl, 3-methylcyclohexyl, 4-methylcyclohexyl, cis-2,5-dimethylcyclohexyl, trans-2,5-dimethylcyclohexyl, 2,2,5,5-tetramethylcyclohexyl, 2-methoxycyclopentyl, 2-methoxycyclohexyl, 20           3-methoxycyclopentyl, 3-methoxycyclohexyl, 2-chlorocyclopentyl, 3-chlorocyclopentyl, 2,4-dichlorocyclopentyl, 2,2,4,4-tetrachlorocyclopentyl, 2-chlorocyclohexyl, 3-chlorocyclohexyl, 4-chlorocyclohexyl, 25           2,5-dichlorocyclohexyl, 2,2,5,5-tetrachlorocyclohexyl, 2-thiomethylcyclopentyl, 2-thiomethylcyclohexyl, 3-thiomethylcyclopentyl, 3-thiomethylcyclohexyl and further derivatives;
  - 30       - C<sub>6</sub>-C<sub>14</sub> aryl, examples being phenyl, 1-naphthyl, 2-naphthyl, 1-anthryl, 2-anthryl, 9-anthryl, 1-phenanthryl, 2-phenanthryl, 3-phenanthryl, 4-phenanthryl and 9-phenanthryl, preferably phenyl, 1-naphthyl and 2-naphthyl, with particular preference phenyl;
  - 35       - C<sub>6</sub>-C<sub>14</sub> aryl such as phenyl, 1-naphthyl, 2-naphthyl, 1-anthryl, 2-anthryl, 9-anthryl, 1-phenanthryl, 2-phenanthryl, 3-phenanthryl, 4-phenanthryl and 9-phenanthryl, substituted by one or more
  - 40           - C<sub>1</sub>-C<sub>12</sub> alkyl groups, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, sec-pentyl, neo-pentyl, 1,2-dimethylpropyl, iso-amyl, n-hexyl, iso-hexyl, sec-hexyl, 45           n-heptyl, iso-heptyl, n-octyl, n-nonyl, n-decyl, and n-dodecyl; preferably C<sub>1</sub>-C<sub>6</sub> alkyl such as methyl, ethyl, n-propyl, iso-propyl,

- n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, sec-pentyl, neo-pentyl, 1,2-dimethylpropyl, iso-amyl, n-hexyl, iso-hexyl, sec-hexyl, with particular preference C<sub>1</sub>-C<sub>4</sub> alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl and tert-butyl;
- 5
- C<sub>1</sub>-C<sub>12</sub> alkyl groups in turn substituted by a hydrophilic group X; examples are -CH<sub>2</sub>-CH<sub>2</sub>-SO<sub>3</sub><sup>-</sup>,  
 10 - (CH<sub>2</sub>)<sub>10</sub>-SO<sub>3</sub><sup>-</sup>, - (CH<sub>2</sub>)<sub>12</sub>-SO<sub>3</sub><sup>-</sup>, - (CH<sub>2</sub>)<sub>16</sub>-SO<sub>3</sub><sup>-</sup>,  
 - (CH<sub>2</sub>)<sub>18</sub>-SO<sub>3</sub><sup>-</sup>, -CH<sub>2</sub>-NMe<sub>3</sub><sup>+</sup>, - (CH<sub>2</sub>)<sub>10</sub>-NMe<sub>3</sub><sup>+</sup>,  
 - (CH<sub>2</sub>)<sub>12</sub>-NMe<sub>3</sub><sup>+</sup>, - (CH<sub>2</sub>)<sub>16</sub>-NMe<sub>3</sub><sup>+</sup>, - (CH<sub>2</sub>)<sub>18</sub>-NMe<sub>3</sub><sup>+</sup>,  
 -CH<sub>2</sub>-(O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>2</sub>-OH, -CH<sub>2</sub>-(O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>3</sub>-OH,  
 -CH<sub>2</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>)<sub>4</sub>-OH, -O-(CH<sub>2</sub>-CH<sub>2</sub>)<sub>5</sub>-OH,  
 15 -CH<sub>2</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>)<sub>6</sub>-OH or -CH<sub>2</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>)<sub>8</sub>-OH;
  - halogens, such as fluorine, chlorine, bromine and iodine, chlorine and bromine being preferred;
  - monohalogenated or polyhalogenated C<sub>1</sub>-C<sub>12</sub> alkyl  
 20 groups such as fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, bromomethyl, dibromomethyl, tribromomethyl, pentafluoroethyl, perfluoropropyl and perfluorobutyl, particular preference being given to fluoromethyl,  
 25 difluoromethyl, trifluoromethyl and perfluorobutyl;
  - C<sub>1</sub>-C<sub>12</sub> alkoxy groups, preferably C<sub>1</sub>-C<sub>6</sub> alkoxy groups such as methoxy, ethoxy, n-propoxy,  
 30 iso-propoxy, n-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, n-pentoxy, iso-pentoxy, n-hexoxy and iso-hexoxy, with particular preference methoxy, ethoxy, n-propoxy and n-butoxy;
  - silyloxy groups OSiR<sup>10</sup>R<sup>11</sup>R<sup>12</sup>, R<sup>10</sup> to R<sup>12</sup> being  
 35 selected independently of one another from hydrogen, C<sub>1</sub>-C<sub>6</sub> alkyl groups, benzyl radicals and C<sub>6</sub>-C<sub>14</sub> aryl groups; preference is given to the trimethylsilyloxy, triethylsilyloxy, triisopropylsilyloxy, diethylisopropylsilyloxy,  
 40 dimethylhexylsilyloxy, tert-butyldimethylsilyloxy, tert-butyldiphenylsilyloxy, tribenzylsilyloxy, triphenylsilyloxy and the tri-para-xylylsilyloxy groups; particular preference is given to the trimethylsilyloxy  
 45 group and the tert-butyldimethylsilyloxy group;

- 5 or amino groups  $\text{NR}^{13}\text{R}^{14}$ ,  $\text{R}^{13}$  and  $\text{R}^{14}$  being selected independently of one another from hydrogen,  $\text{C}_1\text{-C}_6$  alkyl groups, benzyl groups and  $\text{C}_6\text{-C}_{14}$  aryl groups, which may form a saturated or unsaturated 5- to 10-membered ring; preference is given to the dimethylamino, the diethylamino, the diisopropylamino, the methylphenylamino group and the diphenylamino group. Examples of amino groups with saturated rings are the *N*-piperidyl group and the *N*-pyrrolidinyl group; examples of amino groups with unsaturated rings are the *N*-pyrryl group, the *N*-indolyl group and the *N*-carbazolyl group;
- 10
- 15  $\text{C}_1\text{-C}_{12}$  alkoxy groups, preferably  $\text{C}_1\text{-C}_6$  alkoxy groups such as methoxy, ethoxy, *n*-propoxy, iso-propoxy, *n*-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, *n*-pentoxy, iso-pentoxy, *n*-hexoxy and iso-hexoxy, with particular preference methoxy, ethoxy, *n*-propoxy and *n*-butoxy;
- 20 silyloxy groups  $\text{OSiR}^{10}\text{R}^{11}\text{R}^{12}$ ,  $\text{R}^{10}$  to  $\text{R}^{12}$  being selected independently of one another from hydrogen,  $\text{C}_1\text{-C}_6$  alkyl groups, benzyl radicals and  $\text{C}_6\text{-C}_{14}$  aryl groups; preference is given to the trimethylsilyloxy, triethylsilyloxy, triisopropylsilyloxy, diethylisopropylsilyloxy, dimethylhexylsilyloxy, tert-butyl dimethylsilyloxy, tert-butyl diphenylsilyloxy, tribenzylsilyloxy, triphenylsilyloxy and the tri-para-xylylsilyloxy groups; particular preference is given to the
- 25 trimethylsilyloxy group and the tert-butyl dimethylsilyloxy group;
- 30
- 35 halogens, such as fluorine, chlorine, bromine and iodine, chlorine and bromine being preferred;
- 40 or amino groups  $\text{NR}^{13}\text{R}^{14}$ ,  $\text{R}^{13}$  and  $\text{R}^{14}$  being selected independently of one another from hydrogen,  $\text{C}_1\text{-C}_6$  alkyl groups and  $\text{C}_6\text{-C}_{14}$  aryl groups, which may form a saturated or unsaturated 5- to 10-membered ring; preference is given to the dimethylamino, the diethylamino, the diisopropylamino, the methylphenylamino group and the diphenylamino group. Examples of amino groups with saturated rings are the *N*-piperidyl group and the *N*-pyrrolidinyl group; examples of amino groups with unsaturated rings are the *N*-pyrryl group, the
- 45 *N*-indolyl group and the *N*-carbazolyl group;

it being possible for the radicals  $R^2$  and  $R^3$  together with the carbon atoms of the parent structure to form a 5- to 8-membered ring. Possible examples of  $R^2$  and  $R^3$  together are the following:

- 5  $-(CH_2)_3-$  (trimethylene),  $-(CH_2)_4-$  (tetramethylene),  $-(CH_2)_5-$  (pentamethylene),  $-(CH_2)_6-$  (hexamethylene),  $-CH_2-CH=CH-$ ,  
 $-CH_2-CH=CH-CH_2-$ ,  $-CH=CH-CH=CH-$ ,  $-O-CH_2-O-$ ,  $-O-CHMe-O-$ ,  
 $-O-CH-(C_6H_5)-O-$ ,  $-O-CH_2-CH_2-O-$ ,  $-O-CMe_2-O-$ ,  $-NMe-CH_2-CH_2-NMe-$ ,  
 $-NMe-CH_2-NMe-$  or  $-O-SiMe_2-O-$

10 and at least one radical  $R^2$  or  $R^3$  carrying a hydrophilic group X.

$R^4$  to  $R^7$  are:

- 15 - hydrogen,  
 - hydrophilic groups X,  
 -  $C_1-C_{12}$  alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, sec-pentyl, neo-pentyl, 1,2-dimethylpropyl, iso-amyl, n-hexyl,  
 20 iso-hexyl, sec-hexyl, n-heptyl, iso-heptyl, n-octyl, n-nonyl, n-decyl, and n-dodecyl; preferably  $C_1-C_6$  alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, sec-pentyl, neo-pentyl, 1,2-dimethylpropyl,  
 25 iso-amyl, n-hexyl, iso-hexyl, sec-hexyl, with particular preference  $C_1-C_4$  alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl and tert-butyl,  
 30 -  $C_1-C_{12}$  alkyl substituted one or more times by identical or different substituents from the group consisting of halogens,  $C_1-C_{12}$  alkoxy groups and  $C_1-C_{12}$  thioether groups, these groups being as defined above;  
 35 -  $C_1-C_{12}$  alkyl groups in turn substituted by a hydrophilic group X; examples are  $CH_2-CH_2-SO_3^-$ ,  $-(CH_2)_{10}-SO_3^-$ ,  $-(CH_2)_{12}-SO_3^-$ ,  $-(CH_2)_{16}-SO_3^-$ ,  $-(CH_2)_{18}-SO_3^-$ ,  $-CH_2-NMe_3^+$ ,  $-(CH_2)_{10}-NMe_3^+$ ,  $-(CH_2)_{12}-NMe_3^+$ ,  $-(CH_2)_{16}-NMe_3^+$ ,  $-(CH_2)_{18}-NMe_3^+$ ,  
 40  $CH_2-(O-CH_2-CH_2)_2-OH$ ,  $-CH_2-(O-CH_2-CH_2)_3-OH$ ,  $CH_2-O-(CH_2-CH_2)_4-OH$ ,  $-O-(CH_2-CH_2)_5-OH$ ,  $CH_2-O-(CH_2-CH_2)_6-OH$  or  $CH_2-O-(CH_2-CH_2)_8-OH$   
 -  $C_7-C_{13}$  aralkyl, preferably  $C_7$  to  $C_{12}$  phenylalkyl such as benzyl, 1-phenethyl, 2-phenethyl,  
 45 1-phenylpropyl, 2-phenylpropyl, 3-phenylpropyl,

- neophyl (1-methyl-1-phenylethyl), 1-phenylbutyl, 2-phenylbutyl, 3-phenylbutyl and 4-phenylbutyl, with particular preference benzyl;
- 5        - C<sub>3</sub>-C<sub>12</sub> cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl and cyclododecyl; cyclopentyl, cyclohexyl and cycloheptyl are preferred;
- 10       - among the substituted cycloalkyl groups, mention may be made by way of example of the following:
- 15       2-methylcyclopentyl, 3-methylcyclopentyl, cis-2,4-dimethylcyclopentyl, trans-2,4-dimethylcyclopentyl, 2,2,4,4-tetramethylcyclopentyl, 2-methylcyclohexyl, 3-methylcyclohexyl, 4-methylcyclohexyl, cis-2,5-dimethylcyclohexyl, trans-2,5-dimethylcyclohexyl, 2,2,5,5-tetramethylcyclohexyl, 2-methoxycyclopentyl, 2-methoxycyclohexyl,
- 20       3-methoxycyclopentyl, 3-methoxycyclohexyl, 2-chlorocyclopentyl, 3-chlorocyclopentyl, 2,4-dichlorocyclopentyl, 2,2,4,4-tetrachlorocyclopentyl, 2-chlorocyclohexyl, 3-chlorocyclohexyl, 4-chlorocyclohexyl, 2,5-dichlorocyclohexyl,
- 25       2,2,5,5-tetrachlorocyclohexyl, 2-thiomethylcyclopentyl, 2-thiomethylcyclohexyl, 3-thiomethylcyclopentyl, 3-thiomethylcyclohexyl and further derivatives;
- 30       - C<sub>6</sub>-C<sub>14</sub> aryl, examples being phenyl, 1-naphthyl, 2-naphthyl, 1-anthryl, 2-anthryl, 9-anthryl, 1-phenanthryl, 2-phenanthryl, 3-phenanthryl, 4-phenanthryl and 9-phenanthryl, preferably phenyl, 1-naphthyl and 2-naphthyl, with particular
- 35       preference phenyl;
- 40       - C<sub>6</sub>-C<sub>14</sub> aryl such as phenyl, 1-naphthyl, 2-naphthyl, 1-anthryl, 2-anthryl, 9-anthryl, 1-phenanthryl, 2-phenanthryl, 3-phenanthryl, 4-phenanthryl and 9-phenanthryl, substituted by one or more
- 45       - C<sub>1</sub>-C<sub>12</sub> alkyl groups, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, sec-pentyl, neo-pentyl, 1,2-dimethylpropyl, iso-amyl, n-hexyl, iso-hexyl, sec-hexyl, n-heptyl, iso-heptyl, n-octyl, n-nonyl, n-decyl, and n-dodecyl; preferably C<sub>1</sub>-C<sub>6</sub> alkyl such as methyl, ethyl, n-propyl, iso-propyl,



- n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, sec-pentyl, neo-pentyl, 1,2-dimethylpropyl, iso-amyl, n-hexyl, iso-hexyl, sec-hexyl, with particular preference C<sub>1</sub>-C<sub>4</sub> alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl and tert-butyl;
- 5
- 10
- 15
- 20
- 25
- 30
- 35
- 40
- 45
- C<sub>1</sub>-C<sub>12</sub> alkyl groups in turn substituted by a hydrophilic group X; examples are -CH<sub>2</sub>-CH<sub>2</sub>-SO<sub>3</sub><sup>-</sup>, -(CH<sub>2</sub>)<sub>10</sub>-SO<sub>3</sub><sup>-</sup>, -(CH<sub>2</sub>)<sub>12</sub>-SO<sub>3</sub><sup>-</sup>, -(CH<sub>2</sub>)<sub>16</sub>-SO<sub>3</sub><sup>-</sup>, -(CH<sub>2</sub>)<sub>18</sub>-SO<sub>3</sub><sup>-</sup>, -CH<sub>2</sub>-NMe<sub>3</sub><sup>+</sup>, -(CH<sub>2</sub>)<sub>10</sub>-NMe<sub>3</sub><sup>+</sup>, -(CH<sub>2</sub>)<sub>12</sub>-NMe<sub>3</sub><sup>+</sup>, -(CH<sub>2</sub>)<sub>16</sub>-NMe<sub>3</sub><sup>+</sup>, -(CH<sub>2</sub>)<sub>18</sub>-NMe<sub>3</sub><sup>+</sup>, -CH<sub>2</sub>-(O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>2</sub>-OH, -CH<sub>2</sub>-(O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>3</sub>-OH, -CH<sub>2</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>)<sub>4</sub>-OH, -CH<sub>2</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>)<sub>5</sub>-OH, -CH<sub>2</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>)<sub>6</sub>-OH or -CH<sub>2</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>)<sub>8</sub>-OH;
  - halogens, such as fluorine, chlorine, bromine and iodine, chlorine and bromine being preferred;
  - NO<sub>2</sub> groups,
  - hydrophilic groups X,
  - monohalogenated or polyhalogenated C<sub>1</sub>-C<sub>12</sub> alkyl groups such as fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, bromomethyl, dibromomethyl, tribromomethyl, pentafluoroethyl, perfluoropropyl and perfluorobutyl, particular preference being given to fluoromethyl, difluoromethyl, trifluoromethyl and perfluorobutyl;
  - C<sub>1</sub>-C<sub>12</sub> alkoxy groups, preferably C<sub>1</sub>-C<sub>6</sub> alkoxy groups such as methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, n-pentoxo, iso-pentoxo, n-hexoxy and iso-hexoxy, with particular preference methoxy, ethoxy, n-propoxy and n-butoxy;
  - silyloxy groups OSiR<sup>10</sup>R<sup>11</sup>R<sup>12</sup>, R<sup>10</sup> to R<sup>12</sup> being selected independently of one another from hydrogen, C<sub>1</sub>-C<sub>6</sub> alkyl groups, benzyl radicals and C<sub>6</sub>-C<sub>14</sub> aryl groups; preference is given to the trimethylsilyloxy, triethylsilyloxy, triisopropylsilyloxy, diethylisopropylsilyloxy, dimethylhexylsilyloxy, tert-butyl dimethylsilyloxy, tert-butyl diphenylsilyloxy, tribenzylsilyloxy, triphenylsilyloxy and the

- tri-para-xylylsilyloxy groups; particular preference is given to the trimethylsilyloxy group and the tert-butyldimethylsilyloxy group;
- 5 - or amino groups  $NR^{13}R^{14}$ ,  $R^{13}$  and  $R^{14}$  being selected independently of one another from hydrogen,  $C_1$ - $C_6$  alkyl groups, benzyl groups and  $C_6$ - $C_{14}$  aryl groups, which may form a saturated or unsaturated 5- to 10-membered ring;
- 10 preference is given to the dimethylamino, the diethylamino, the diisopropylamino, the methylphenylamino group and the diphenylamino group. Examples of amino groups with saturated rings are the *N*-piperidyl group and the *N*-pyrrolidinyl group; examples of amino groups
- 15 with unsaturated rings are the *N*-pyrryl group, the *N*-indolyl group and the *N*-carbazolyl group;
- $C_1$ - $C_{12}$  alkoxy groups, preferably  $C_1$ - $C_6$  alkoxy groups such as methoxy, ethoxy, *n*-propoxy, iso-propoxy, *n*-butoxy, iso-butoxy, sec-butoxy, tert-butoxy,
- 20 *n*-pentoxy, iso-pentoxy, *n*-hexoxy and iso-hexoxy, with particular preference methoxy, ethoxy, *n*-propoxy and *n*-butoxy;
- silyloxy groups  $OSiR^{10}R^{11}R^{12}$ ,  $R^{10}$  to  $R^{12}$  being selected independently of one another from
- 25 hydrogen,  $C_1$ - $C_6$  alkyl groups, benzyl radicals and  $C_6$ - $C_{14}$  aryl groups; preference is given to the trimethylsilyloxy, triethylsilyloxy, triisopropylsilyloxy, diethylisopropylsilyloxy, dimethylhexylsilyloxy, tert-butyldimethylsilyloxy,
- 30 tert-butyldiphenylsilyloxy, tribenzylsilyloxy, triphenylsilyloxy and the tri-para-xylylsilyloxy groups; particular preference is given to the trimethylsilyloxy group and the tert-butyldimethylsilyloxy group;
- 35 - halogens, such as fluorine, chlorine, bromine and iodine, chlorine and bromine being preferred;
- $NO_2$  groups
- or amino groups  $NR^{13}R^{14}$ ,  $R^{13}$  and  $R^{14}$  being selected independently of one another from hydrogen,  $C_1$ - $C_6$  alkyl groups and  $C_6$ - $C_{14}$  aryl groups, which may form
- 40 a saturated or unsaturated 5- to 10-membered ring; preference is given to the dimethylamino, the diethylamino, the diisopropylamino, the methylphenylamino group and the diphenylamino group. Examples of amino groups with saturated rings are the *N*-piperidyl group and the
- 45 *N*-pyrrolidinyl group; examples of amino groups with

unsaturated rings are the *N*-pyrryl group, the *N*-indolyl group and the *N*-carbazolyl group;

it being possible for pairs of adjacent radicals  $R^4$  to  $R^7$  together with the carbon atoms of the parent aromatic to form a 5- to 8-membered ring which may carry further substituents  $Z$ . Possible examples of  $R^4$  and  $R^5$  together are the following:  $-(CH_2)_3-$  (trimethylene),  $-(CH_2)_4-$  (tetramethylene),  $-(CH_2)_5-$  (pentamethylene),  $-(CH_2)_6-$  (hexamethylene),  $-CH_2-CH=CH-$ ,  $-CH_2-CH=CH-CH_2-$ ,  $-CH=CH-CH=CH-$ ,  $-O-CH_2-O-$ ,  $-O-CHMe-O-$ ,  $-O-CH-(C_6H_5)-O-$ ,  $-O-CH_2-CH_2-O-$ ,  $-O-CMe_2-O-$ ,  $-NMe-CH_2-CH_2-NMe-$ ,  $-NMe-CH_2-NMe-$  or  $-O-SiMe_2-O-$ .

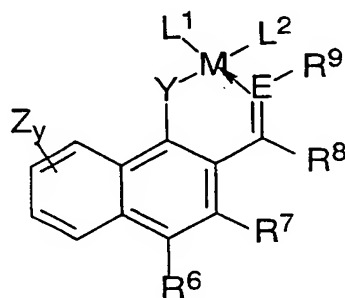
$R^8$  and  $R^9$  are chosen from:

- 15                    -  $C_1-C_{12}$  alkyl groups unsubstituted or substituted by a hydrophilic group  $X$ ; examples of unsubstituted  $C_1-C_{12}$  alkyl groups are methyl, ethyl, *n*-propyl, iso-propyl, *n*-butyl, iso-butyl, sec-butyl, tert-butyl, *n*-pentyl, iso-pentyl, sec-pentyl, neo-pentyl, 1,2-dimethylpropyl, iso-amyl, *n*-hexyl, iso-hexyl, sec-hexyl, *n*-heptyl, iso-heptyl, *n*-octyl, *n*-nonyl, *n*-decyl, and *n*-dodecyl; preferably  $C_1-C_6$  alkyl such as methyl, ethyl, *n*-propyl, iso-propyl, *n*-butyl, iso-butyl, sec-butyl, tert-butyl, *n*-pentyl, iso-pentyl, sec-pentyl, neo-pentyl, 1,2-dimethylpropyl, iso-amyl, *n*-hexyl, iso-hexyl, sec-hexyl, with particular preference  $C_1-C_4$  alkyl such as methyl, ethyl, *n*-propyl, iso-propyl, *n*-butyl, iso-butyl, sec-butyl and tert-butyl.
- 20                    Examples of the  $C_1-C_{12}$  alkyl groups substituted by a hydrophilic group  $X$  are  $CH_2-SO_3^-$ ,  $CH_2-CH_2-SO_3^-$ ,  $-(CH_2)_{10}-SO_3^-$ ,  $-(CH_2)_{12}-SO_3^-$ ,  $-(CH_2)_{16}-SO_3^-$ ,  $-(CH_2)_{18}-SO_3^-$ ,  $-CH_2-NMe_3^+$ ,  $-(CH_2)_{10}-NMe_3^+$ ,  $-(CH_2)_{12}-NMe_3^+$ ,  $-(CH_2)_{16}-NMe_3^+$ ,  $-(CH_2)_{18}-NMe_3^+$ ,  $-CH_2-O-CH_2-CH_2-OH$ ,  $-CH_2-O-(CH_2-CH_2)_2-OH$ ,  $CH_2-O-(CH_2-CH_2)_3-OH$ ,  $-CH_2-O-(CH_2-CH_2)_4-OH$ ,  $-CH_2-O-(CH_2-CH_2)_5-OH$ ,  $-CH_2-O-(CH_2-CH_2)_6-OH$ , or  $-CH_2-O-(CH_2-CH_2)_8-OH$ ;
- 25                    -  $C_7-C_{13}$  aralkyl radicals unsubstituted or substituted by a hydrophilic group  $X$ ; examples of unsubstituted aralkyl radicals are  $C_7$  to  $C_{12}$  phenylalkyl such as benzyl, 1-phenethyl, 2-phenethyl, 1-phenylpropyl, 2-phenylpropyl, 3-phenylpropyl, neophyl (1-methyl-1-phenylethyl), 1-phenylbutyl, 2-phenylbutyl, 3-phenylbutyl and 4-phenylbutyl,
- 30
- 35
- 40
- 45

with particular preference benzyl; preferred examples of the aralkyl radicals substituted by a hydrophilic group X are meta-benzylsulfonate, para-benzylsulfonate, ortho-HO(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-O-benzyl, meta-HO(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-O-benzyl and para-HO(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-O-benzyl, n being an integer between 1 and 15, preferably from 2 to 10 and with particular preference from 3 to 8.

- C<sub>6</sub>-C<sub>14</sub> aryl groups unsubstituted or substituted by a hydrophilic group X; examples of unsubstituted C<sub>6</sub>-C<sub>14</sub> aryl groups are phenyl, 1-naphthyl, 2-naphthyl, 1-anthryl, 2-anthryl, 9-anthryl, 1-phenanthryl, 2-phenanthryl, 3-phenanthryl, 4-phenanthryl and 9-phenanthryl, preferably phenyl, 1-naphthyl and 2-naphthyl, with particular preference phenyl; examples of C<sub>6</sub>-C<sub>14</sub> aryl groups substituted by hydrophilic groups X are meta-benzosulfonate, ortho-benzosulfonate, para-benzosulfonate, α-(4-naphthosulfonate), β-(4-naphthosulfonate), ortho-HO(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-O-phenyl, meta-HO(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-O-phenyl and para-HO(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-O-phenyl, n being an integer between 1 and 15, preferably from 2 to 10 and with particular preference from 3 to 8.

In one particular embodiment of the process, complexes of the formula Ib' are used



Ib'

where the substituents Z can be identical or different and are selected from the following groups:

- hydrogen;
- halogen such as fluorine, chlorine, bromine and iodine, preferably fluorine or chlorine;
- C<sub>1</sub>-C<sub>4</sub> alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl and tert-butyl;
- hydrophilic groups X, X being as defined above,
- NO<sub>2</sub>,

- C<sub>1</sub>-C<sub>4</sub> alkoxy such as methoxy, ethoxy, n-propoxy, n-butoxy and tert-butoxy.

One or more radicals R<sup>4</sup> to R<sup>9</sup> may carry identical or different hydrophilic groups X. Preference is given to those embodiments of the process in which at least one or two or more radicals R<sup>4</sup> to R<sup>9</sup> carries/carry a hydrophilic group X.

R<sup>10</sup> to R<sup>15</sup> are selected independently of one another from

10

- hydrogen,
- C<sub>1</sub>-C<sub>20</sub> alkyl groups, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, sec-pentyl, neo-pentyl, 1,2-dimethylpropyl, iso-amyl, n-hexyl, iso-hexyl, sec-hexyl, n-octyl, n-nonyl, iso-nonyl, n-decyl, iso-decyl, n-undecyl, iso-undecyl, n-dodecyl, iso-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl and n-eicosyl; with particular preference C<sub>1</sub>-C<sub>4</sub> alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl and tert-butyl;
- C<sub>1</sub>-C<sub>20</sub> alkyl groups substituted by O(C<sub>1</sub>-C<sub>6</sub> alkyl) or N(C<sub>1</sub>-C<sub>6</sub> alkyl)<sub>2</sub> radicals, such as for example CH<sub>2</sub>-CH<sub>2</sub>-OCH<sub>3</sub> or CH<sub>2</sub>-CH<sub>2</sub>-NMe<sub>2</sub>;
- C<sub>3</sub>-C<sub>12</sub> cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl and cyclododecyl; cyclopentyl, cyclohexyl and cycloheptyl are preferred;
- C<sub>7</sub>-C<sub>13</sub> aralkyl radicals, preferably C<sub>7</sub> to C<sub>12</sub> phenylalkyl such as benzyl, 1-phenethyl, 2-phenethyl, 1-phenylpropyl, 2-phenylpropyl, 3-phenylpropyl, neophyl (1-methyl-1-phenylethyl), 1-phenylbutyl, 2-phenylbutyl, 3-phenylbutyl and 4-phenylbutyl, with particular preference benzyl;
- C<sub>6</sub>-C<sub>14</sub> aryl groups, such as phenyl, 1-naphthyl, 2-naphthyl, 1-anthryl, 2-anthryl, 9-anthryl, 1-phenanthryl, 2-phenanthryl, 3-phenanthryl, 4-phenanthryl and 9-phenanthryl, preferably phenyl, 1-naphthyl and 2-naphthyl, with particular preference phenyl;

it being possible for pairs of adjacent radicals R<sup>10</sup> to R<sup>15</sup> to form, together with the relevant heteroatom, a 5- to 8-membered ring. Possible examples of R<sup>10</sup> and R<sup>11</sup> together are the following: -(CH<sub>2</sub>)<sub>3</sub>- (trimethylene), -(CH<sub>2</sub>)<sub>4</sub>- (tetramethylene), -(CH<sub>2</sub>)<sub>5</sub>-

(pentamethylene),  $-(CH_2)_6-$  (hexamethylene),  $-CH_2-CH=CH-$ ,  
 $-CH_2-CH=CH-CH_2-$ ,  $-CH=CH-CH=CH-$ ,  $-O-CH_2-O-$ ,  $-O-CHMe-O-$ ,  
 $-O-CH-(C_6H_5)-O-$ ,  $-O-CH_2-CH_2-O-$ ,  $-O-CMe_2-O-$ ,  $-NMe-CH_2-CH_2-NMe-$ ,  
 $-NMe-CH_2-NMe-$  or  $-O-SiMe_2-O-$ ;

5

$R^{16}$  are identical or different are chosen from

- hydrogen,
- $C_1-C_{20}$  alkyl groups, such as methyl, ethyl,  
 10 n-propyl, iso-propyl, n-butyl, iso-butyl,  
 sec-butyl, tert-butyl, n-pentyl, iso-pentyl,  
 sec-pentyl, neo-pentyl, 1,2-dimethylpropyl,  
 iso-amyl, n-hexyl, iso-hexyl, sec-hexyl, n-octyl,  
 n-nonyl, iso-nonyl, n-decyl, iso-decyl, n-undecyl,  
 iso-undecyl, n-dodecyl, iso-dodecyl, n-tetradecyl,  
 15 n-hexadecyl, n-octadecyl and n-eicosyl; with  
 particular preference  $C_1-C_4$  alkyl such as methyl,  
 ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl,  
 sec-butyl and tert-butyl;
- $C_1-C_{20}$  alkyl groups substituted by  $O(C_1-C_6 \text{ alkyl})$  or  
 20  $N(C_1-C_6 \text{ alkyl})_2$  radicals, such as for example  
 $CH_2-CH_2-OCH_3$  or  $CH_2-CH_2-NMe_2$ ;
- $C_3-C_{12}$  cycloalkyl such as cyclopropyl, cyclobutyl,  
 cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl,  
 cyclononyl, cyclodecyl, cycloundecyl and  
 25 cyclododecyl; cyclopentyl, cyclohexyl and  
 cycloheptyl are preferred;
- $C_7-C_{13}$  aralkyl radicals, preferably  $C_7$  to  $C_{12}$   
 phenylalkyl such as benzyl, 1-phenethyl,  
 2-phenethyl, 1-phenylpropyl, 2-phenylpropyl,  
 30 3-phenylpropyl, neophyl (1-methyl-1-phenylethyl),  
 1-phenylbutyl, 2-phenylbutyl, 3-phenylbutyl and  
 4-phenylbutyl, with particular preference benzyl;
- $C_6-C_{14}$  aryl groups, such as phenyl, 1-naphthyl,  
 2-naphthyl, 1-anthryl, 2-anthryl, 9-anthryl,  
 1-phenanthryl, 2-phenanthryl, 3-phenanthryl,  
 35 4-phenanthryl and 9-phenanthryl, preferably phenyl,  
 1-naphthyl and 2-naphthyl, with particular  
 preference phenyl; unsubstituted or substituted by  
 a hydrophilic group X.

40

For compounds of the formula Ia or Ib with ionic hydrophilic  
 groups, counterions are necessary in order to compensate the  
 electrical charge. For electrostatic compensation of negative  
 charges such as  $-SO_3^-$  or  $-O-PO_3^{2-}$ , cations of the alkali metals  
 45 such as  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$  and  $Cs^+$  have proven suitable, preference  
 being given to  $Na^+$  and  $K^+$  on account of their lower price. Also  
 suitable are ammonium salts with cations of the formula  $NR^{15}_2H_{4-2}$ ,

$R^{15}$  being as described above and  $z$  being an integer from 0 to 4. Particularly preferred ammonium ions are  $[NH_4]^+$ ,  $[NEt_2H_2]^+$ ,  $[NMe_4]^+$ ,  $[HN(n-C_4H_9)_3]^+$ ,  $[N(n-C_4H_9)_4]^+$ ,  $[n-C_{16}H_{33}NMe_3]^+$  and  $[C_6H_5-NHMe_2]^+$ .

5

For electrostatic compensation of positive charges such as  $NH(R^{15})_2^+$  or  $N(R^{15})_3^+$ , a large number of anions have proven suitable. Examples that may be mentioned include the following: halides such as fluoride, chloride, bromide or iodide; and also  
 10 hydrogen sulfate, triflate  $CF_3SO_3^-$ , acetate,  $BF_4^-$ ,  $[B(C_6H_5)_4]^-$ ,  $[B(C_6F_5)_4]^-$  or  $PF_6^-$  or  $SbF_6^-$ , preference being given to chloride and hydrogen sulfate.

It is also possible for the complex of formula Ia or Ib to carry  
 15 two different hydrophilic groups, namely an anionic group selected from  $-SO_3^-$  and  $-O-PO_3^{2-}$  and a cationic group selected from  $NH(R^{15})_2^+$  or  $N(R^{15})_3^+$ , so that the zwitterionic complex is electrically neutral.

20 Selected, very particularly preferred compounds of the formula Ia are:

$Na^+ [Ni(Ph)PPh_3(\kappa^2P, OPh_2PC(SO_3^-)=C(-O)(p-MeC_6H_4))] \text{ (formula Ia.1, see Working Example)}$

25

$[n-C_{16}H_{33}NMe_3]^+ [Ni(Ph)PPh_3(\kappa^2P, OPh_2PC(SO_3^-)=C(-O)(p-MeC_6H_4))] \text{ (formula Ia.2, see Working Example)}$

$Na^+ [Ni(Ph)PPh_3(\kappa^2P, O(o-MeC_6H_4)_2PC(SO_3^-)=C(-O)(p-MeC_6H_4))]$

30

$[n-C_{16}H_{33}NMe_3]^+ [Ni(Ph)PPh_3(\kappa^2P, OPh_2PC(SO_3^-)=C(-O)(p-MeC_6H_4))]$

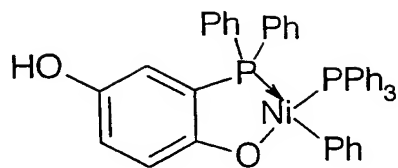
$Na^+ [Ni(Ph)PPh_3(\kappa^2P, OPh_2PC(SO_3^-)=C(-O)(p-MeC_6H_4))]$

35 where Me = methyl and Ph = phenyl,

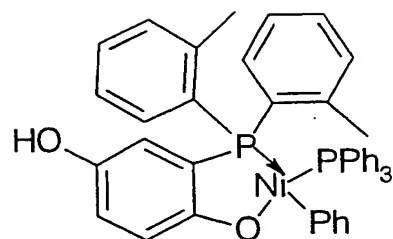
and also the compounds depicted below of the formula Ia.3 to Ia.10:

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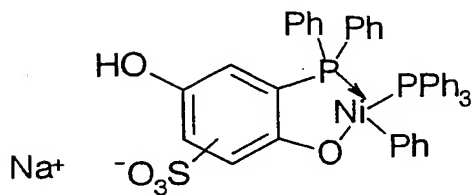
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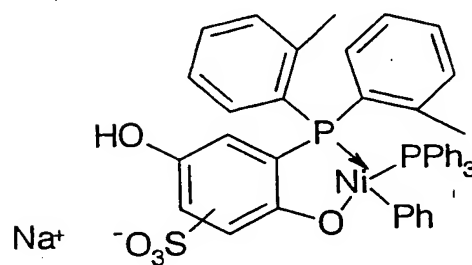
Ia.3



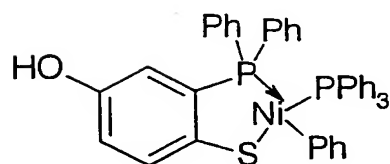
Ia.4



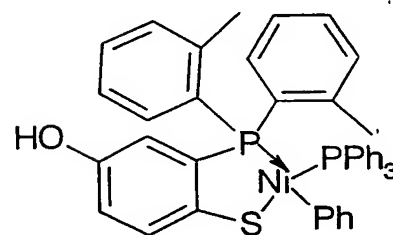
Ia.5



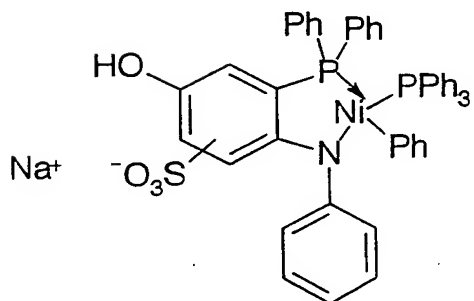
Ia.6



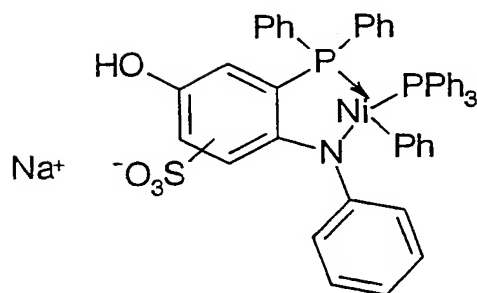
Ia.7



Ia.8



Ia.9



Ia.10

Selected, very particularly preferred compounds of the formula Ib  
45 are:



25

[O-3,5-I<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-O-C(H)-N=C2,6(*i*-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] Ni(C<sub>6</sub>H<sub>5</sub>)(PPh<sub>3</sub>) (formula Ib.1, see Working Example)

[O-3,5-I<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-O-CMe-N=C2,6(*i*-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] Ni(C<sub>6</sub>H<sub>5</sub>)(PPh<sub>3</sub>)

5

[O-3-(9-anthracenyl)C<sub>6</sub>H<sub>3</sub>-O-C(H)-N=C2,6(*i*-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]Ni(C<sub>6</sub>H<sub>5</sub>)(PPh<sub>3</sub>)

[O-3-(9-anthracenyl)-5-NO<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>-O-C(H)-N=C2,6(*i*-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]-  
Ni(C<sub>6</sub>H<sub>5</sub>)(PPh<sub>3</sub>)

10

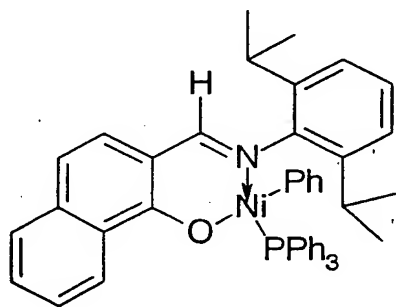
Na<sup>+</sup> [O-3-(9-anthracenyl)-5-(SO<sub>3</sub><sup>-</sup>)-C<sub>6</sub>H<sub>2</sub>-O-C(H)-N=C2,6(*i*-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]  
Ni(C<sub>6</sub>H<sub>5</sub>)(PPh<sub>3</sub>)

[O-3-(9-anthracenyl)-5-I-C<sub>6</sub>H<sub>2</sub>-O-C(H)-N=C2,6(*i*-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]Ni(C<sub>6</sub>H<sub>5</sub>)-

15 (PPh<sub>3</sub>)

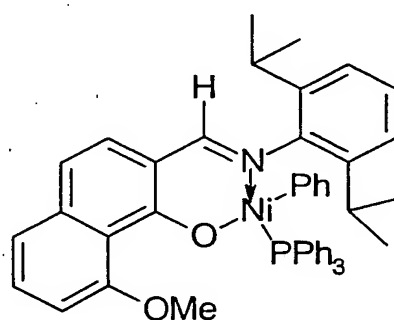
and also the compounds depicted below of the formulae Ib'.1 to Ib'.10.

20



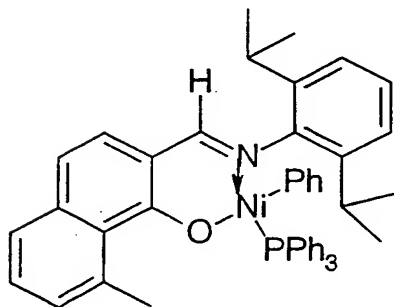
Ib'.1

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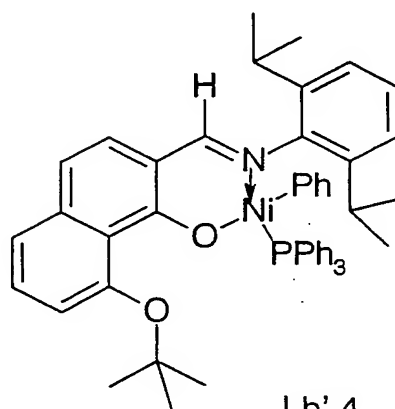
Ib'.2

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Ib'.3

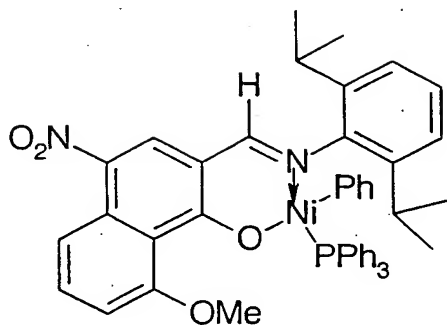
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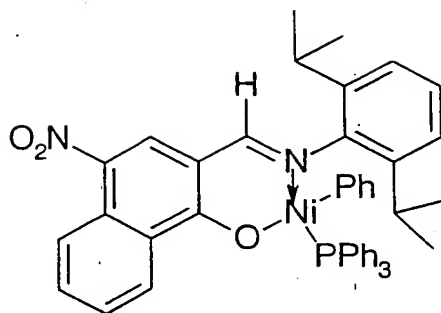
Ib'.4

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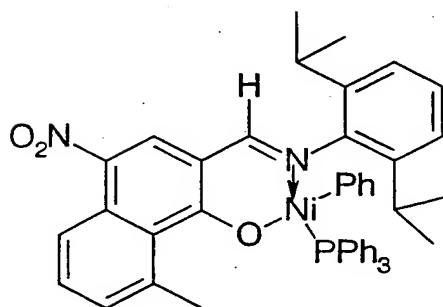
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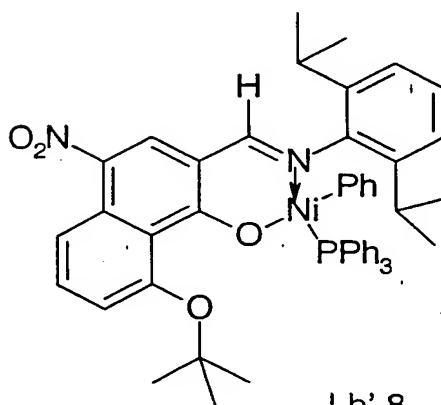
Ib'.5



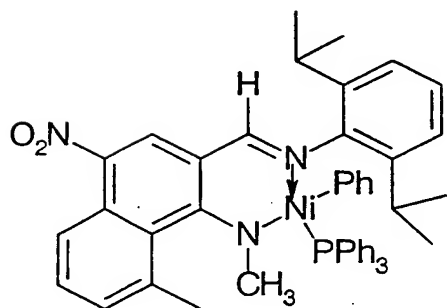
Ib'.6



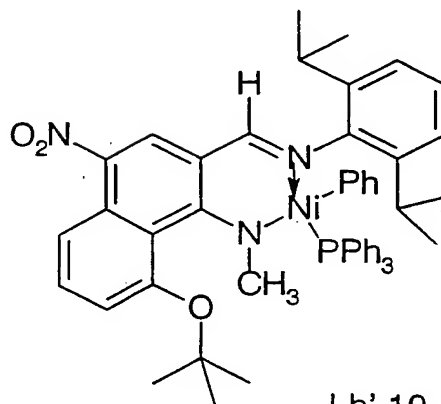
Ib'.7



Ib'.8



Ib'.9



Ib'.10

40 The synthesis of the complexes of the formula Ia and Ib is known per se. Synthesis procedures for complexes of the formula Ia can be found in EP-A 0 046 331, EP-A 0 046 328 and EP-A 0 052 929. Procedures for the synthesis of complexes of the formula Ib can be found in the applications WO 98/30609 and WO 98/42664 and in  
45 the publication by C. Wang et al., *Organometallics* 1998, 17, 3149. The sulfonations were in each case conducted in accordance with the formulation described by N. A. Nesmeyanov et al. in

Dokl. Akad. Nauk SSSR 1963, 151, 856. For the nomenclature of the compounds of the formula Ib, the nomenclature used is that in analogy to WO 98/42664.

- 5 The compounds Ia and Ib may be used in a ratio of from 0 : 100 to 100 : 0 mol%. Preferred embodiments are 0 : 100 mol%, 10 : 90 mol%, 50 : 50 mol%, 90 : 10 mol% and 100 : 0 mol%.

- Numerous complexes of the formula Ia or b are polymerization-  
10 inactive by themselves. They require an activator, which is commonly supposed to abstract the ligand  $L^1$ . Said activator may comprise olefin complexes of rhodium or of nickel.

- Preferred nickel (olefin)<sub>y</sub> complexes available commercially from  
15 Aldrich are  $Ni(C_2H_4)_3$ ,  $Ni(1,5\text{-cyclooctadiene})_2$  " $Ni(COD)_2$ ",  $Ni(1,6\text{-cyclododecadiene})_2$ , or  $Ni(1,5,9\text{-all-trans-cyclododecatriene})_2$ . Particular preference is given to  $Ni(COD)_2$ .

- Particularly suitable are mixed ethylene/1,3-dicarbonyl complexes  
20 of rhodium, examples being rhodium acetylacetonate-ethylene  $Rh(acac)(CH_2=CH_2)_2$ , rhodium benzoylacetonate-ethylene  $Rh(C_6H_5-CO-CH-CO-CH_3)(CH_2=CH_2)_2$  or  $Rh(C_6H_5-CO-CH-CO-C_6H_5)(CH_2=CH_2)_2$ . The most suitable is  $Rh(acac)(CH_2=CH_2)_2$ . This compound may be synthesized in accordance with the formulation of R. Cramer from  
25 *Inorg. Synth.* 1974, 15, 14.

- Some complexes of the formula Ia or b may be activated by ethylene. The ease of the activation reaction depends critically on the nature of the ligand  $L^1$ . For instance, where  $L^1$  is a  
30 tetramethylethylenediamine ligand it has been found that no activator is required.

The polymerization of the 1-olefins using the metal complexes of the invention may be carried out in a manner known per se.

- 35 The sequence of addition of the reagents for the polymerization is not critical. For instance, gaseous monomer may be injected onto the solvent or liquid monomer metered in, first of all, and the catalyst is added subsequently. Alternatively, the catalyst  
40 solution may first be diluted with further solvent, and monomer added subsequently.

- The actual polymerization usually runs under a minimum pressure of 1 bar; below this pressure, the polymerization rate is too  
45 low. Preference is given to 2 bar, while a minimum pressure of 10 bar is particularly preferred.

4000 bar may be mentioned as the maximum pressure; at higher pressures, the requirements imposed on the material of the polymerization reactor are very high, and the process becomes uneconomic. Preference is given to 100 bar, and particular  
5 preference to 50 bar.

The polymerization temperature may be varied within a wide range. 10°C may be specified as the minimum temperature, since at lower temperatures the rate of polymerization falls. Preference is  
10 given to a minimum temperature of 40°C, and particular preference to 65°C. As the maximum practicable temperature, it is possible to specify 350°C and preferably 150°C; particular preference is given to 100°C.

15 Prior to the polymerization, the complexes are dissolved in an organic solvent or in water. Several minutes' stirring or shaking ensure that the solution is clear. The stirring time may be between 1 and 100 minutes, depending on the solubility of the structure in question.

20 At the same time, the activator, if required, is dissolved in a second portion of the same solvent or else in acetone.

Suitable organic solvents are aromatic solvents such as benzene,  
25 toluene, ethylbenzene, ortho-xylene, meta-xylene and para-xylene, and mixtures thereof. Also suitable are cyclic ethers such as tetrahydrofuran and dioxane or acyclic ethers such as diethyl ether, di-n-butyl ether, diisopropyl ether or 1,2-dimethoxyethane. Ketones as well, such as acetone, methyl ethyl ketone or  
30 diisobutyl ketone, are suitable, likewise amides such as dimethylformamide or dimethylacetamide. Furthermore, mixtures of these solvents with one another are suitable, as are mixtures of these solvents with water or with alcohols such as methanol or ethanol.

35 Preference is given to acetone and water and to mixtures of acetone and water, the proportion being arbitrary.

The amount of the solvent is likewise not critical; however, it  
40 is necessary to ensure that the complex and the activator are able to dissolve completely - otherwise, losses of activity may be expected. If desired, the dissolution process may be accelerated by means of ultrasonic treatment.

The emulsifier for optional addition may be dissolved in a third portion of the solvent or else may be dissolved together with the complex.

- 5 The amount of the emulsifier is chosen such that the mass ratio between monomer and emulsifier is greater than 1, preferably greater than 10 and with particular preference greater than 20. The less the amount of emulsifier that need be used, the better.
- 10 The complexes of the formula Ia and Ib may themselves act as emulsifiers. The polymerization activity, however, is significantly increased if an additional emulsifier is added. This emulsifier may be nonionic or ionic in nature.
- 15 Customary nonionic emulsifiers are, for example, ethoxylated mono-, di- and tri-alkylphenols (EO units: ie 3 to 50, alkyl: C<sub>4</sub>-C<sub>12</sub>) and also ethoxylated fatty alcohols (EO units: 3 to 80; alkyl: C<sub>8</sub>-C<sub>36</sub>). Examples thereof are the Lutensol® grades from BASF AG or the Triton® grades from Union Carbide.
- 20 Customary anionic emulsifiers are, for example, alkali metal salts and ammonium salts of alkyl sulfate (alkyl: C<sub>8</sub> to C<sub>12</sub>), of sulfuric monoesters with ethoxylated alkanols (EO units: 4 to 30, alkyl: C<sub>12</sub>-C<sub>18</sub>) and with ethoxylated alkylphenols (EO units: 3 to 50, alkyl: C<sub>4</sub>-C<sub>12</sub>), of alkylsulfonic acids (alkyl: C<sub>12</sub>-C<sub>18</sub>) and of
- 25 alkylarylsulfonic acids (alkyl: C<sub>9</sub>-C<sub>18</sub>).

- Suitable cationic emulsifiers are, in general, C<sub>6</sub>-C<sub>18</sub> alkyl-, C<sub>6</sub>-C<sub>18</sub> aralkyl- or heterocycle-containing primary, secondary, tertiary or quaternary ammonium salts, alkanolammonium salts,
- 30 pyridinium salts, imidazolinium salts, oxazolinium salts, morpholinium salts, thiazolinium salts, and also salts of amine oxides, quinolinium salts, isoquinolinium salts, tropylium salts, sulfonium salts, and phosphonium salts. Examples that may be mentioned include dodecylammonium acetate or the corresponding
  - 35 hydrochloride, the chlorides or acetates of the various 2-(N,N,N-trimethylammonium)ethylparaffinic esters, N-cetylpyridinium chloride, N-laurylpyridinium sulfate, and N-cetyl-N,N,N-trimethylammonium bromide, N-dodecyl-N,N,N-trimethylammonium bromide,
  - 40 N,N-distearyl-N,N-dimethylammonium chloride, and the gemini surfactant N,N'-(lauryldimethyl)ethylenediamine dibromide. Numerous further examples can be found in H. Stache, *Tensid-Taschenbuch*, Carl-Hanser-Verlag, Munich, Vienna, 1981 and in McCutcheon's *Emulsifiers & Detergents*, MC Publishing Company,
  - 45 Glen Rock, 1989.

Subsequently, the components - complex in solution, optionally the solution of the emulsifier, and optionally the solution of the activator - are placed in the polymerization reactor.

Polymerization reactors which have proven useful are stirred  
5 vessels and autoclaves and also tube reactors, it being possible for the tube reactors to be configured as loop reactors.

The monomer or monomers to be polymerized is or are mixed in the polymerization medium. Said polymerization medium may comprise  
10 water or mixtures of water with the abovementioned solvents. It should be ensured that the proportion of water is at least 50% by volume, based on the total mixture, preferably at least 90% by volume and with particular preference at least 95% by volume.

15 The solutions of the complex, of the activator if appropriate and of the emulsifier if appropriate are combined with the mixture of monomer and aqueous polymerization medium. The sequence of the addition of the various components is not critical per se. However, it is necessary for the components to be combined with  
20 sufficient rapidity that there is no crystallization of any poorly soluble complex compounds which may occur as intermediates.

Suitable polymerization processes include in principle both  
25 continuous and batchwise processes. Preference is given to semicontinuous (semi-batch) processes, in which, after all of the components have been mixed, monomer or monomer mixtures is or are metered in subsequently in the course of the polymerization.

30 In accordance with the process of the invention, aqueous polymer dispersions are initially obtained.

The average diameters of the polymer particles in the dispersions of the invention are from 10 to 1000 nm, preferably from 50 to  
35 500 nm and with particular preference from 70 to 350 nm. The distribution of the particle diameters may, but need not be, very uniform. For certain applications, especially those with high solids contents (> 55%), broad or bimodal distributions are in fact preferred.

40

The polymers obtained in accordance with the process of the invention have technically advantageous properties. In the case of polyethylene, they have a high degree of crystallinity, as may be demonstrated, for example, by the number of branches. Less  
45 than 40 branches, preferably less than 20 branches per 1000 carbon atoms of the polymer, and with particular preference less

than 10 branches are found, as determined by  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectroscopy.

The enthalpies of fusion of the polyethylenes obtainable by the process of the invention are greater than 100 J/g, preferably greater than 140 and with particular preference greater than 180 J/g, measured by DSC.

The molecular weight distributions of the polyethylenes obtainable by the process of the invention are narrow, i.e., the Q values are from 1.1 to 3.5, preferably from 1.5 to 3.1.

An advantage of the dispersions of the invention, in addition to the favorable price owing to the inexpensive monomers and processes, is that they are more stable to weathering than are dispersions of polybutadiene or butadiene copolymers. Relative to dispersions of polymers containing acrylates or methacrylates as principal monomer, the reduced tendency to undergo hydrolysis is an advantage that may be mentioned. Also advantageous is that the majority of olefins are highly volatile and unpolymerized residual monomers can easily be removed. A final advantage is that there is no need to add molecular mass regulators such as tert-dodecyl mercaptan, for example, during the polymerization, which on the one hand are difficult to separate off and on the other hand have an unpleasant odor.

From the aqueous dispersions obtained initially, it is possible by removing the water and any organic solvent or solvents to obtain the polymer particles as such. Numerous common techniques are suitable for removing the water and any organic solvent or solvents, examples being filtration, spray drying, and evaporation. The polymers obtained in this way possess a good morphology and a high bulk density.

The particle size may be determined using light scattering methods. An overview is given in D. Distler (editor) "Wäßrige Polymerdispersionen", Wiley-VCH Verlag, 1st edition, 1999, Chapter 4.

The dispersions of the invention may be used to advantage in numerous applications, such as, for example, paper applications such as paper coating or surface sizing, and also in paints and varnishes, chemicals for the construction industry, adhesive base materials, molded foams, textile and leather applications, carpet back coatings, mattresses, and pharmaceutical applications.

Paper coating is the coating of the paper surface with aqueous pigmented dispersions. In this case, the dispersions of the invention are advantageous on account of their favorable price. Surface sizing is the pigment-free application of hydrophobicizing substances. In this case, the polyolefin dispersions, as particularly hydrophobic substances, which have to date been difficult to obtain under economic conditions, are of particular advantage. A further advantage is that during the preparation of the dispersions of the invention for paper coating or surface sizing there is no need to add any molecular mass regulators such as tert-dodecyl mercaptan, for example, which on the one hand are difficult to separate off and on the other hand have an unpleasant odor.

In paints and varnishes the dispersions of the invention are particularly suitable because their pricing is very favorable. Aqueous polyethylene dispersions are particularly advantageous, because in addition they also have a particular UV stability. Aqueous polyethylene dispersions are also particularly suitable because they are resistant to chemicals, which are common in chemicals for the construction industry.

In adhesives, especially in adhesives for self-adhesive labels or films and also plasters, but also in construction adhesives or industrial adhesives, the dispersions of the invention have economic advantages. In construction adhesives in particular they are especially favorable because they are resistant to basic chemicals, which are common in chemicals for the construction industry. In molded foams which can be produced from the dispersions of the invention by processes known per se such as the Dunlop process or the Talalay process, the favorable price of the dispersions of the invention is again advantageous. Further components used are gelling agents, soaps, thickeners, and vulcanizing pastes. Molding foams are processed, for example, into mattresses.

Textile and leather applications serve to durabilize and enhance textile or leather. Among the effects, mention may be made by way of example of the impregnation and the further finishing of the textiles. An advantage of the dispersions of the invention as a constituent in textile and leather applications, besides the favorable price, is the freedom from odor, since olefins as residual monomers can be removed easily.

Carpet back coatings are used to bond the carpet fiber to the backing, and also have the function of giving the carpet the necessary rigidity and of providing uniform distribution of



additives such as flame retardants or antistats, for example. An advantage of the dispersions of the invention besides the favorable price is their insensitivity to the common additives. In particular, the polyethylene dispersions of the invention have  
5 proven to be particularly inert chemically. Finally, it is advantageous that during the preparation of the dispersions of the invention for carpet back coatings there is no need to add molecular mass regulators such as tert-dodecyl mercaptan, for example, which on the one hand are difficult to separate off and  
10 on the other hand have an unpleasant odor.

By pharmaceutical preparations are meant dispersions as vehicles for drugs. Dispersions as vehicles for drugs are known per se. Advantages of the dispersions of the invention as vehicles for  
15 drugs include the economically favorable price and their resistance to physiological influences such as gastric fluid or enzymes.

#### Working Examples

20

General notes: unless otherwise described, the syntheses were carried out in accordance with the Schlenk technique in the absence of air and moisture.

25 Tetrahydrofuran, toluene, dichloromethane, diethyl ether and pentane were rendered absolute before being used (dichloromethane: calcium hydride; others: sodium) and distilled under argon.

30 The viscosity measurements on the polymers were carried out in accordance with ISO 1628-3. The molecular mass determinations were carried out by means of GPC. In accordance with DIN 55672, the conditions chosen were as follows: solvent 1,2,4-trichlorobenzene, flow rate: 1 ml/min; temperature: 140°C. Measurement was  
35 carried out on a Waters 150C instrument which had been calibrated with polyethylene standards.

#### 1. Ligand synthesis $[\text{C}_{16}\text{H}_{33}\text{NMe}_3]^+ [\text{Ph}_3\text{P}-\text{C}(\text{H})(\text{SO}_3^-)\text{C}(=\text{O})-4-\text{MeC}_6\text{H}_4]^-$

##### 40 1.1 Preparation of $\text{Ph}_3\text{P}=\text{CHC}(=\text{O})-4-\text{MeC}_6\text{H}_4$

17.8 g of methyltriphenylphosphonium bromide (49.8 mmol) were introduced as an initial charge under argon and suspended in 80 ml of tetrahydrofuran. 27.8 ml of a 1.6 M solution of butyl-  
45 lithium in hexane (corresponding to 44.4 mmol of butyllithium) were injected into this suspension with stirring. Clarification of the suspension and a color change from yellow to red were

observed. The solution was subsequently stirred for 60 minutes until the starting material was completely dissolved, and then a solution of 3.87 g (25 mmol) of p-toluenesulfonyl chloride in 10 ml of tetrahydrofuran was injected. This produced a yellow  
5 discoloration and the precipitation of a white solid. The reaction mixture was then stirred for 2 hours before being poured into 400 ml of water, and the resulting suspension was extracted with five times 150 ml of diethyl ether. The combined organic phases were dried over sodium sulfate, filtered and subsequently  
10 concentrated intensively. The solution was stored at 4°C overnight and the pale yellow precipitated solid was filtered off with suction (4 g, 10.1 mmol). The mother liquor was concentrated even more intensively and cooled again. This gave a further 1.5 g (3.8 mmol) of product, so that the overall yield of  
15  $\text{Ph}_3\text{P}=\text{CHC}(=\text{O})-4-\text{MeC}_6\text{H}_4$  was 5.5 g (13.9 mmol, 56%).

#### 1.2 Preparation of $\text{Ph}_3\text{P}^+-\text{C}(\text{H})(\text{SO}_3^-)-\text{C}(=\text{O})-4-\text{MeC}_6\text{H}_4$

2.1 g (13.2 mmol) of sulfur trioxide-pyridine adduct were  
20 introduced as an initial charge under an argon atmosphere. A solution of 5 g (12.7 mmol) of  $\text{Ph}_3\text{P}=\text{CHC}(=\text{O})-4-\text{MeC}_6\text{H}_4$  in 40 ml of methylene chloride was added slowly dropwise with ice cooling. Within a few minutes a yellow solution was formed, which was stirred at room temperature overnight. Subsequently, the solvent  
25 was stripped off, and the colorless residue obtained was stirred in 30 ml of ethanol, filtered off with suction and washed with twice 15 ml of ethanol. Drying under reduced pressure gave 4.5 g (9.5 mmol) of  $\text{Ph}_3\text{P}^+-\text{C}(\text{H})(\text{SO}_3^-)-\text{C}(=\text{O})-4-\text{MeC}_6\text{H}_4$  as a colorless powder in 75% yield.

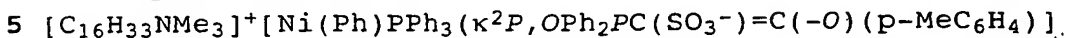
30

#### 1.3 Preparation of $[\text{C}_{16}\text{H}_{33}\text{NMe}_3]^+[\text{Ph}_3\text{P}=\text{C}(\text{SO}_3^-)-\text{C}(=\text{O})-4-\text{MeC}_6\text{H}_4]$

3.87 g (8.17 mmol) of  $\text{Ph}_3\text{P}^+-\text{C}(\text{H})(\text{SO}_3^-)-\text{C}(=\text{O})-4-\text{MeC}_6\text{H}_4$  were suspended in 50 ml of a 2:1 methanol/water mixture and titrated  
35 with hexadecyltrimethylammonium hydroxide solution (10% in water) using 1 drop of 1% strength ethanolic phenolphthalein solution as indicator. The pH was additionally monitored using pH-fix indicator paper. Toward the end of the titration, the suspension was heated to 50°C and titration was continued until finally a  
40 clear solution (pH = 7.5) was obtained. The solvent was subsequently stripped off and traces of water were removed by azeotropic distillation with ethanol. This and drying under an oil pump vacuum gave 5.16 g (6.81 mmol) of  $[\text{C}_{16}\text{H}_{33}\text{NMe}_3]^+[\text{Ph}_3\text{P}=\text{C}(\text{SO}_3^-)-\text{C}(=\text{O})-4-\text{MeC}_6\text{H}_4]$  as a colorless hygroscopic solid in  
45 83% yield.

The similar ligand  $\text{Na}^+[\text{Ph}_3\text{P}=\text{C}(\text{SO}_3^-)-\text{C}(=\text{O})-4-\text{MeC}_6\text{H}_4]$  was obtained using aqueous sodium hydroxide solution for the neutralization.

## 2. Complex synthesis

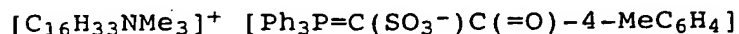


The synthesis was carried out under an argon atmosphere employing the standard Schlenk technique. 709 mg (2.58 mmol) of  $\text{Ni}(\text{COD})_2$  were suspended in 25 ml of tetrahydrofuran at  $-30^\circ\text{C}$ , 1 equivalent (676 mg) of triphenylphosphine was added with stirring, and the appearance of a red coloration was observed. A solution of 1 equivalent (1.954 g) of the ligand  $[\text{C}_{16}\text{H}_{33}\text{NMe}_3]^+[\text{Ph}_3\text{P}=\text{C}(\text{SO}_3^-)-\text{C}(=\text{O})-4-\text{MeC}_6\text{H}_4]$  in 25 ml of THF, heated beforehand to  $50^\circ\text{C}$  in order to dissolve the ligand completely, was injected (using a transfer cannula) with stirring into the reaction mixture obtained by adding the triphenylphosphine. The mixture was allowed to warm to room temperature and then heated briefly to  $50^\circ\text{C}$ , after which the dark solution was stirred overnight at room temperature. Finally, the solvent was removed under reduced pressure, the residue was taken up in 50 ml of toluene and filtered, and the filtrate was concentrated under reduced pressure to about 1/5 of its volume. The toluenic phase was combined with 70 ml of pentane and the precipitate formed was filtered off. It was subsequently washed a number of times with pentane and dried under reduced pressure to give 2.453 g (2.27 mmol) of the complex  $[\text{C}_{16}\text{H}_{33}\text{NMe}_3]^+[\text{Ni}(\text{Ph})\text{PPh}_3(\kappa^2\text{P}, \text{OPh}_2\text{PC}(\text{SO}_3^-)=\text{C}(-\text{O})(\text{p-MeC}_6\text{H}_4))]$  in 88% yield as a yellow solid.

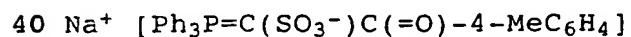
The analogous sodium complex  $\text{Na}^+[\text{Ni}(\text{Ph})\text{PPh}_3(\kappa^2\text{P}, \text{OPh}_2\text{PC}(\text{SO}_3^-)=\text{C}(-\text{O})(\text{p-MeC}_6\text{H}_4))]$  was obtained using the ylide ligand  $\text{Na}^+[\text{Ph}_3\text{P}=\text{C}(\text{SO}_3^-)-\text{C}(=\text{O})-4-\text{MeC}_6\text{H}_4]$ , in which case there was no need to warm the reaction mixture.

Characteristic NMR data:

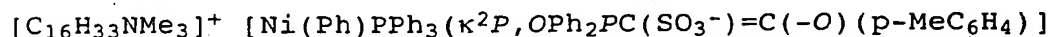
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$^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ , 200 MHz, externally 85% strength  $\text{H}_3\text{PO}_4$ )  $\delta$  16.8 (s)



$^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ , 200 MHz, externally 85% strength  $\text{H}_3\text{PO}_4$ )  $\delta$  16.7 (s)



45

$^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ , 200 MHz, externally 85% strength  $\text{H}_3\text{PO}_4$ )  $\delta$  38.3 (d,  $^2\text{J}(\text{P},\text{P}) = 136.4$  Hz),  $\delta$  21.0 (d,  $^2\text{J}(\text{P},\text{P}) = 136.4$  Hz)

$\text{Na}^+[\text{Ni}(\text{Ph})\text{PPh}_3(\kappa^2\text{P},\text{OPh}_2\text{PC}(\text{SO}_3^-)=\text{C}(-\text{O})(\text{p-MeC}_6\text{H}_4))]$

5

$^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ , 200 MHz, externally 85% strength  $\text{H}_3\text{PO}_4$ )  $\delta$  35.4 (d,  $^2\text{J}(\text{P},\text{P}) = 138.7$  Hz),  $\delta$  21.0 (d,  $^2\text{J}(\text{P},\text{P}) = 138.8$  Hz)

### 3. Polymerization Examples

10

#### 3.1 General notes

The polymerization experiments were conducted in a steel autoclave (Büchi-Miniclave), temperature regulation was carried out externally using a poly(ethylene glycol) heating bath, the stirring speed (propeller stirrer) was 1000 rpm, and the total liquid phase volume was 100 ml in each case. In the transfer operations, a portion of the solvent volume was used for rinsing, and the solutions/suspensions were prepared under argon. For polymerizations in the presence of water, the water was degassed beforehand by passing argon through it for several hours; the same applies to the organic solvents used if they were not employed in dried form (see above).

#### 25 3.1.1 Polymerization with

$\text{Na}^+[\text{Ni}(\text{Ph})\text{PPh}_3(\text{Ph}_2\text{PCH}(\text{SO}_3^-)\text{C}(=\text{O})(\text{p-MeC}_6\text{H}_4))]$

The complex was dissolved (together if desired with the emulsifier, e.g., Triton<sup>®</sup> X-100 (1 g), sodium dodecyl sulfate (500 mg), hexadecyltrimethylammonium tetrafluoroborate (357 mg)) in 95 ml of water (in experiments with 50 ml of acetone, 30 ml of acetone was added to the aqueous complex solution) or 50 ml of organic solvent and the solution was stirred for 20 minutes (in order to ensure intimate contact between complex and water prior to the polymerization). Separately from this,  $\frac{1}{2}$  equivalent of acetylacetonatobis(ethylene)rhodium(I) was dissolved in 5 or 50 ml of the respective organic solvent (in the case of experiments with 50 ml of acetone, in 20 ml of acetone). Both solutions were subsequently transferred in succession (first activator, then complex) into the ethylene-flushed autoclave in countercurrent to the ethylene. The autoclave was then flushed a number of times with ethylene gas before the desired ethylene pressure was injected with stirring and the reactor was set to the appropriate temperature.

45

Following reaction, the autoclave was cooled with an ice bath and then let down.

### 3.1.2 Polymerization with $[C_{16}H_{33}NMe_3]^+$

5  $[Ni(Ph)PPh_3(Ph_2PCH(SO_3^-)C(=O)(p-MeC_6H_4))]$

The solutions were prepared under argon. The catalyst was dissolved in half the volume of organic solvent, the appropriate amount of water was injected into this solution if desired, and  
10 then the mixture was stirred for 20 minutes (in order to ensure intimate contact between complex and water prior to the polymerization). Separately from this,  $\frac{1}{2}$  equivalent of acetylacetonatobis(ethylene)rhodium(I) was dissolved in the other half. Both solutions were subsequently transferred in succession  
15 (first activator, second complex) into the ethylene-flushed autoclave in countercurrent to the ethylene and then any remaining volume of water was injected. The autoclave was then flushed a number of times with ethylene gas before the desired ethylene pressure was injected with stirring and the reactor was  
20 set to the appropriate temperature.

The polymerizations were in each case conducted under a pressure of 50 bar; the reaction time was 2 hours.

25 Following reaction, the autoclave was cooled with an ice bath and then let down.

The results can be found in Table 1.

## 30 3.2 Workup

### 3.2.1 Workup of batches without added emulsifier

Solid constituents were filtered off with suction and washed with  
35 methanol or acetone before being dried in a vacuum drying oven at  $50^\circ C$ . In some experiments, the filtrate was concentrated in order to analyze it for dissolved products.

### 3.2.2 Workup of batches with added emulsifier

40 The emulsion obtained was first, where necessary, filtered with suction through a filter paper or glass wool, then filtered through glass wool. The particle diameters were determined using a Malvern Zetasizer. The emulsion was then poured into 200 ml of  
45 acetone and after half an hour of stirring the precipitated solid was filtered off with suction. The resultant solid was washed

with methanol or acetone before being dried in a vacuum drying oven at 50°C.

#### 4. Copolymerization examples: copolymerization of ethylene with norbornene

##### 4.1. Polymerization in water/toluene systems

##### 4.1.1. Use of the complex

10  $[\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]^+[\text{Ni}(\text{Ph})(\text{PPh}_3)(\kappa^2\text{P},\text{OPh}_2\text{PC}(\text{SO}_3^-)=\text{C}(-\text{O})(\text{p-MeC}_6\text{H}_4))]$   
(I a.2)

Solutions of 10.9 mg (4.2  $\mu\text{mol}$ ) of acetylacetonatobis(ethylene)-rhodium(I) and also of 91.0 mg (84.3  $\mu\text{mol}$ ) of  $[\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]^+$   
15  $[\text{Ni}(\text{Ph})(\text{PPh}_3)(\kappa^2\text{P},\text{OPh}_2\text{PC}(\text{SO}_3^-)=\text{C}(-\text{O})(\text{p-MeC}_6\text{H}_4))]$  were prepared separately from one another, each in 5 ml of toluene. Then 85 ml of water and the two solutions were transferred in succession in an ethylene countercurrent into an ethylene-flushed 250 ml steel autoclave with mechanical stirrer mechanism. A solution of 4.0 g  
20 (4.2 mmol) of norbornene in 5 ml of toluene was added. The autoclave was flushed with ethylene a number of times and then an ethylene pressure of 40 bar was injected with stirring (propeller stirrer, 1000 rpm).

25 After the reaction mixture had been stirred at room temperature for three hours, the excess pressure was let off and the solid formed was isolated by decanting and dried under reduced pressure at 50°C (1 g). The polymer obtained is a sticky amorphous material. No precipitation of further polymeric products was  
30 observed when the liquid phases were combined with methanol.

##### 4.1.2. Use of the complex

$[\text{Ni}(\text{Ph})(\text{PPh}_3)(\kappa^2\text{N},\text{O}(2-\text{O}-(3,5-\text{I}_2)-\text{C}_6\text{H}_2)-\text{C}(\text{H})=\text{N}-2,6-(\text{i-Pr})_2-\text{C}_6\text{H}_3)]$   
(I b.1)

35

Example 8: A solution of 5.0 g (53.1 mmol) of norbornene in 5 ml of toluene and a solution of 500 mg (0.8 mmol) of Triton X-100 in 90 ml of water were combined in ethylene countercurrent in an ethylene-flushed 250 ml steel autoclave with mechanical stirrer  
40 mechanism. Separately, a solution of 5.8 mg (22.6  $\mu\text{mol}$ ) of acetylacetonatobis(ethylene)rhodium(I) together with 42.0 mg (45.1  $\mu\text{mol}$ ) of  $[\text{Ni}(\text{Ph})(\text{PPh}_3)(\kappa^2\text{N},\text{O}(2-\text{O}-(3,5-\text{I}_2)-\text{C}_6\text{H}_2)-\text{C}(\text{H})=\text{N}-2,6-(\text{i-Pr})_2-\text{C}_6\text{H}_3)]$  in 5 ml of toluene was prepared and immediately likewise transferred into the autoclave. The autoclave was  
45 flushed with ethylene a number of times and then an ethylene

pressure of 40 bar was injected with stirring (propeller stirrer, 1000 rpm).

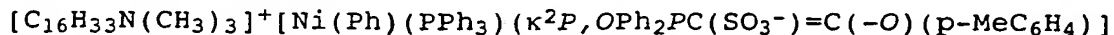
After the reaction mixture had been stirred at room temperature for three hours, the excess pressure was let off. In addition to deposited solid (1.1 g; elastic and transparent) a dispersion was obtained. This dispersion was filtered through glass wool and the particle size was determined by means of static light scattering as being 170 nm. 1.1 g of copolymer were obtained from the dispersion by precipitation with methanol. The norbornene content of this copolymer was determined as being 14 mol% by means of  $^{13}\text{C}$ -NMR (1,1,2,2-tetrachloroethane- $d_2$ , 122°C).

Example 9: A solution of 700 mg (7.4 mmol) of norbornene in 1 ml of toluene and a solution of 1 g (1.6 mmol) of Triton X-100 in 95 ml of water were combined in ethylene countercurrent in an ethylene-flushed 250 ml steel autoclave with mechanical stirrer mechanism. Separately, a solution of 8.7 mg (33.9  $\mu\text{mol}$ ) of acetylacetonatobis(ethylene)rhodium(I) together with 63.0 mg (67.7  $\mu\text{mol}$ ) of  $[\text{Ni}(\text{Ph})(\text{PPh}_3)(\kappa^2\text{N},\text{O}(2\text{-O-(3,5-I}_2\text{)-C}_6\text{H}_2\text{)-C(H)=N-2,6-(i-Pr)}_2\text{-C}_6\text{H}_3)]$  in 4 ml of toluene was prepared and immediately likewise transferred into the autoclave. The autoclave was flushed with ethylene a number of times and then an ethylene pressure of 50 bar was injected with stirring (propeller stirrer, 1000 rpm).

After the reaction mixture had been stirred at room temperature for two hours, the excess pressure was let off. Following filtration through glass wool, a solid was deposited from the resultant polymer dispersion. The batch was introduced into 200 ml of methanol and the copolymer was isolated by filtration and dried under reduced pressure at 50°C (1.3 g). The norbornene content of this copolymer was determined as being 10 mol% by means of  $^{13}\text{C}$ -NMR (1,1,2,2-tetrachloroethane- $d_2$ , 122°C).

#### 4.2. Comparative experiments: Polymerization in pure toluene

Use of the complex



(I. a.2)

Comparative example C10: Solutions of 7.2 mg (27.9  $\mu\text{mol}$ ) of acetylacetonatobis(ethylene)rhodium(I) and also of 60.0 mg (55.6  $\mu\text{mol}$ ) of  $[\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]^+[\text{Ni}(\text{Ph})(\text{PPh}_3)(\kappa^2\text{P},\text{OPh}_2\text{PC}(\text{SO}_3^-)=\text{C}(-\text{O})(\text{p-MeC}_6\text{H}_4))]$  were prepared separately from one another, each in 45 ml of toluene. Then both solutions were transferred in succession in ethylene countercurrent into an

ethylene-flushed 250 ml steel autoclave with mechanical stirrer mechanism. 7.7 g (81.8 mmol) of norbornene, as a solution in 10 ml of toluene, were added. The autoclave was flushed with ethylene a number of times and then an ethylene pressure of 5 10 bar was injected with stirring (propeller stirrer, 1000 rpm).

After the reaction mixture had been stirred at room temperature for three hours, the excess pressure was let off. The clear solution obtained was introduced into 200 ml of methanol and the 10 precipitated copolymer was isolated by decanting and dried under reduced pressure at 50°C (1.5 g). The polymer obtained is transparent. WAXS investigations indicate a degree of crystallinity < 2%.

#### 15 Use of the complex

$[\text{Ni}(\text{Ph})(\text{PPh}_3)(\kappa^2\text{N},\text{O}(2\text{-O}-(3,5\text{-I}_2)\text{-C}_6\text{H}_2)\text{-C}(\text{H})=\text{N}-2,6\text{-(i-Pr)}_2\text{-C}_6\text{H}_3)]$   
(I b.1)

Comparative example C11: Solutions of 11.2 mg (43.4  $\mu\text{mol}$ ) of 20 acetylacetonatobis(ethylene)rhodium(I) and also of 81.0 mg (87.1  $\mu\text{mol}$ ) of  $[\text{Ni}(\text{Ph})(\text{PPh}_3)(\kappa^2\text{N},\text{O}(2\text{-O}-(3,5\text{-I}_2)\text{-C}_6\text{H}_2)\text{-C}(\text{H})=\text{N}-2,6\text{-(i-Pr)}_2\text{-C}_6\text{H}_3)]$  were prepared separately from one another, each in 45 ml of toluene. Then both solutions were transferred in succession in ethylene countercurrent into an 25 ethylene-flushed 250 ml steel autoclave with mechanical stirrer mechanism. 10.0 g (106.2 mmol) of norbornene, as a solution in 10 ml of toluene, were added. The autoclave was flushed with ethylene a number of times and then an ethylene pressure of 10 bar was injected with stirring (propeller stirrer, 1000 rpm).

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After the reaction mixture had been stirred at room temperature for three hours, the excess pressure was let off. The clear solution obtained was introduced into 200 ml of methanol and the precipitated copolymer was isolated by filtration and dried under 35 reduced pressure at 50°C (6 g). The polymer obtained is transparent and elastic. WAXS investigations indicate a degree of crystallinity < 2%.

5. Use of a mixture of  $\text{Na}^+[\text{Ni}(\text{Ph})\text{PPh}_3(\text{Ph}_2\text{PCH}(\text{SO}_3^-)\text{C}(=\text{O})(\text{p-MeC}_6\text{H}_4)]$   
40 (I.a.1) and  $[\text{Ni}(\text{Ph})(\text{PPh}_3)(\kappa^2\text{N},\text{O}(2\text{-O}-(3,5\text{-I}_2)\text{-C}_6\text{H}_2)\text{-C}(\text{H})=\text{N}-2,6\text{-(i-Pr)}_2\text{-C}_6\text{H}_3)]$  (I.b.1) for ethylene polymerization in water (example 12)

1 g of sodium dodecyl sulfate was dissolved under argon in 95 ml 45 of deionized water (degassed by having argon passed through it for several hours) and the solution was transferred in ethylene countercurrent into a multiply ethylene-flushed 250 ml steel



autoclave with mechanical stirrer mechanism. Then, under argon, a solution of 44.0 mg (54  $\mu\text{mol}$ ) of  $\text{Na}^+[\text{Ni}(\text{Ph})\text{PPh}_3(\text{Ph}_2\text{PCH}(\text{SO}_3^-)\text{C}(=\text{O})(\text{p-MeC}_6\text{H}_4))]$ , 60.0 mg (64  $\mu\text{mol}$ ) of  $[\text{Ni}(\text{Ph})(\text{PPh}_3)(\kappa^2\text{N},\text{O}(2-\text{O}-(3,5-\text{I}_2)-\text{C}_6\text{H}_2)-\text{C}(\text{H})=\text{N}-2,6-(\text{i-Pr})_2-\text{C}_6\text{H}_3)]$  and 15.3 mg (59  $\mu\text{mol}$ ) of acetylacetonatobis(ethylene)rhodium(I) in 5 ml of acetone (degassed by having argon passed through it for several hours) was prepared and was immediately likewise transferred into the autoclave. The autoclave was flushed with ethylene gas a number of times, an ethylene pressure of 45 bar was injected with stirring (1000 rpm), and the reactor was conditioned to a temperature of 50°C.

After 2 hours, the autoclave was cooled to room temperature and the polymerization was then terminated by letting down the autoclave. The polyethylene formed was isolated by filtration, washed a number of times with water and also with methanol, and dried in a vacuum drying oven at 50°C (3.2 g).

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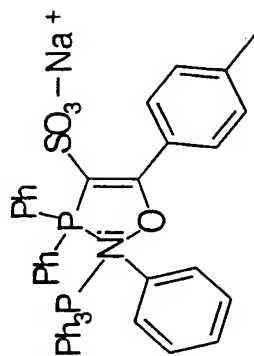
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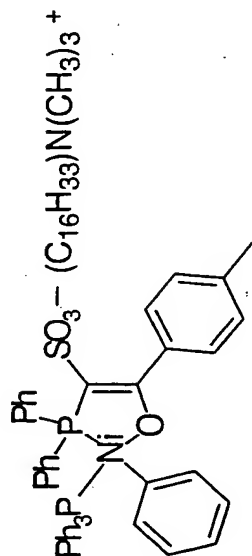
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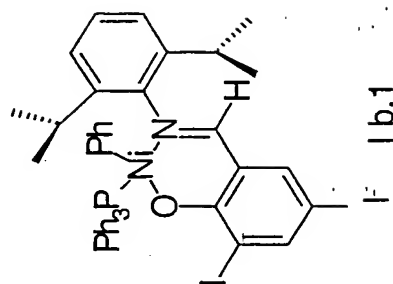
Polymerization results:



1a.1



1a.2



1b.1

Table 1

Example	Reaction conditions			Activity				Polymer analysis				
	Complex	$\mu\text{mol}$ complex	Activator	Solvent volume ratio	Emulsifier	Tem-perature	Yield polymer	kg PE/mol Ni-h	TOF/h	M <sub>w</sub>	Q	$\eta$ value
1	1 a.1	89	Rh(acac)et <sub>2</sub>	Toluene/H <sub>2</sub> O 5:95	-	70 °C	5.9 [g]	33.1	1178	3025 [g]	3.1	0.12 [ml/g]
2	1 a.1	61	Rh(acac)et <sub>2</sub>	Acetone/H <sub>2</sub> O 50:50	-	70	1.8	14.8	517	n.d.	n.d.	0.30
3	1 a.1	108	Rh(acac)et <sub>2</sub>	Acetone/H <sub>2</sub> O 5:95	-	70	2.2	10.1	357	2233	2.3	0.14
4	1 a.1	120	-	Acetone/H <sub>2</sub> O 5:95	1 g Triton X-100	70	1.8	7.5	267	936	1.8	0.08
5	1 a.2	81	Rh(acac)et <sub>2</sub>	Toluene/H <sub>2</sub> O 5:95	-	50	1.2	0.9	32	n.d.	n.d.	0.54
6	1 b.1	19	Rh(acac)et <sub>2</sub>	n-Pentane/H <sub>2</sub> O 10:90	-	70	1.9	50.00	3488	n.d.	n.d.	n.d.

Key: Me: methyl, Ph = phenyl, Rh(acac)et<sub>2</sub> = Rh(acac)(CH<sub>2</sub>=CH<sub>2</sub>)<sub>2</sub>, acac: 2,4-pentanedionato;

PE: polyethylene; n.d.: not determined; TOF: turnover frequency, ratios of the solvents are stated in % by volume.

Table 2: Copolymerization results

Example	Reaction conditions				Activity			Polymer analysis					
	Complex	$\mu\text{mol}$ complex	Activator	Solvent volume ratio	Emulsifier	Tem-perature	Yield polymer	kg polymer/mol Ni-h	M <sub>n</sub>	M <sub>w</sub>	Q	Nor-bornene	T <sub>g</sub>
7	I a.2	84.3	Rh(acac)et <sub>2</sub>	Toluene/H <sub>2</sub> O 85:10	-	25	1.0	4.0	1802	11170	6.2	n.d.	n.d.
8	I b.1	45.1	Rh(acac)et <sub>2</sub>	Toluene/H <sub>2</sub> O 85:15	0.5 g Triton X-100	25	2.2	16.3	88100	186900	2.1	19	-4
9	I b.1	67.7	Rh(acac)et <sub>2</sub>	Toluene/H <sub>2</sub> O 95:5	1 g Triton X-100	25	1.3	9.6	337650	1111300	3.3	10	n.d.
C10	I a.2	55.6	Rh(acac)et <sub>2</sub>	Toluene	-	25	1.5	9.0	1990	15700	7.9	25	25
C11	I b.1	87.1	Rh(acac)et <sub>2</sub>	Toluene	-	25	6.0	23.0	77310	13900	1.8	19	6
12	Ia.1+Ib.1	118	Rh(acac)et <sub>2</sub>	Acetone/H <sub>2</sub> O 95:5	-	50	3.2	13.6	n.d.	n.d.	n.d.	n.d.	n.d.

C10 and C11 are comparative examples without addition of water.

Analysis: degree of crystallinity by WAXS (wide angle X-ray scattering)

$M_w$ ,  $M_n$ : gel permeation chromatography, 1,2,4-trichlorobenzene, 140°C, calibrated with linear polyethylene standards.

Norbornene content: <sup>13</sup>C-NMR spectroscopy, 1,1,2,2-tetrachloroethane-d<sub>2</sub>, all amounts in mol%.